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THE GROWTH AND COLLAPSE OF VAPOR BUBBLES

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ABSTRACT

A theory is developed which describes the behavior of a vapor bubble in a liquid. Its physical basis is the assumption that the heat transfer effects which accompany the evaporation occurring at the bubble wall when the bubble grows, or the condensation that occurs there when the bubble collapses, are dynamically important. The basic equations of hydrodynamics are shown to reduce, for the problem under consideration, to a dynamic equation which describes the behavior of the bubble wall, and a heat convection equation for the liquid which is coupled to the dynamic equation by a boundary condition at the bubble surface. A solution for the heat problem is obtained under the assumption that significant temperature variation in the liquid occurs only in a thin thermal boundary layer surrounding the bubble wall. An estimate of the correction to the temperature solution is also derived. Once the temperature at the bubble wall is given, the vapor pressure within the bubble is known and the dynamic problem becomes determinate.

The theory is applied to the cases of the growth of a vapor bubble in a superheated liquid, and the collapse of a vapor bubble in a liquid below its boiling temperature at the external pressure. The simplifying physical assumptions made in the course of the investigation are justified for the specific example of vapor bubble behavior in water.

A comparison of the theory with experiment is given for the observable range of bubble growth in superheated water, and the agreement is found to be very good.

TABLE OF CONTENTS

Section	Title	Page
I.	INTRODUCTION	1
II.	FORMULATION OF THE PROBLEM	10
	Basic Equations	10
	The Problem in the liquid	12
	The Problem in the Vapor	16
	Boundary Conditions	20
	Conclusion	26
III.	THE HEAT PROBLEM	28
	Convection Solution	29
	Diffusion Solutions	39
	General Comparison of the Convection and Diffusion Solutions	46
	Comparison for Free Bubble Growth	47
IV.	THE DYNAMIC PROBLEM	53
	The Expanding Vapor Bubble	56
	Relaxation Period	58
	Early Phase	62
	Asymptotic Phase	64
	Intermediate Solution	77
	Solution for the Expanding Bubble	81
	The Collapsing Vapor Bubble	84
	APPENDIX	
A.	List of Physical Constants	89
B.	Evaluation of the Diffusion Integrals III(47b), (47c)	90
C.	Early Phase Temperature Integral IV(46)	95
D.	Asymptotic Phase Temperature Integral IV(59)	97
E.	Numerical Solution for the Collapsing Bubble	99
	REFERENCES	103

I. INTRODUCTION

The term cavitation is used to describe the presence of a vapor phase in a region filled predominantly with liquid. The condition necessary for the appearance of cavitation is that locally the vapor pressure of the liquid must exceed the external pressure to which the liquid is subjected; this condition is by no means sufficient to produce cavitation, however, because of the presence of surface stresses in the liquid. These stresses, attributable to the short range attraction of the liquid molecules for one another, tend to reduce any surface element of the liquid to one having the least (mean) curvature consistent with the mechanical constraints imposed on the liquid. Thus, an otherwise unconstrained vapor cavity will be spherical. The resultant of the stresses on an element of surface is a force directed along the normal drawn from the concave side of the element. For a vapor cavity to grow, the vapor pressure must compensate not only the external pressure on the liquid, but also the effective pressure of the surface stresses.

Since the surface stresses increase with the curvature of the surface, there is a minimum possible size for an unconstrained pure vapor bubble existing in the liquid, even at temperatures above the boiling point of the liquid at the prevailing external pressure. Smaller bubbles are unstable against collapse. The question therefore arises as to how a bubble could form initially. The problem of the nucleation of vapor bubbles has been extensively studied in recent years, notahly by Harvey(1) and Pease,(2) in connection with their research in animal physiology. The conclusion drawn from these studies is that in a moderately superheated liquid, the nuclei for cavitation bubbles consist of small permanent gas bubbles in the liquid, or gas pockets stabilized on solid particles. When these are removed from the liquid (by agitation, continued boiling, or by compressing the liquid under pressures great enough to force the gases into solution) cavitation ceases, and can be reintroduced only by subjecting the liquid to extreme tension or high temperature. Thus, water put under a pressure of several hundred atmospheres for a period of a few hours becomes able to withstand negative pressures as great as 150 atm. without rupturing,(3) and can be heated to 270°C before it explodes.(4) The residual nuclei, following degassing, are believed to consist of hydrophobic substances in the liquid or at its surface.(2)

The process involved in the nucleation of a bubble by a permanent gas can be explained by a simple model. Suppose the gas satisfies the perfect gas law. Then the pressure p_g of the gas in the bubble is given in terms of the temperature T and radius R of the bubble by

$$p_g = \frac{NT}{R^3}, \tag{1}$$

where N is a constant, proportional to the number of moles of gas in the bubble. The pressure p_s due to surface tension is

$$p_s = \frac{2\sigma}{R}, \tag{2}$$

σ being the surface tension constant of the liquid. If the bubble is in equilibrium, the vapor pressure is a function of T alone, say $p_{eq}(T)$. Denoting the external pressure by p_∞, one has as the condition of equilibrium that

$$p_g + p_{eq}(T) = p_s + p_\infty. \tag{3}$$

The equilibrium will be stable if the pressure difference $p_g + p_{eq} - p_s - p_\infty$ is a decreasing function of the bubble radius at the point of equilibrium. These conditions are conveniently expressed in terms of a function

$$f_T(R) = \frac{R^3}{T}\left\{ p_\infty + p_s - p_{eq}(T)\right\} = \frac{1}{T}\left\{ [p_\infty - p_{eq}(T)]\, R^3 + 2\sigma R^2\right\}. \tag{4}$$

Thus, for a given gas content N, the equilibrium radius (or radii) R_o of the bubble is given by

$$f_T(R_o) = N, \tag{5}$$

and the condition for stability becomes

$$f_T'(R_o) > 0, \tag{6}$$

where $f_T'(R)$ denotes the derivative of $f_T(R)$ with respect to R.

Below the boiling point of the liquid, $p_\infty - p_{eq} > 0$, and so $f_T(R)$ is an increasing function of R. Thus, there is just one equilibrium radius R_o

of a gas nucleated bubble for a given value of T below the boiling point of the liquid, according to (5), and the equilibrium is stable at that radius by (6). Above the boiling point of the liquid, the coefficient of R^3 in $f_T(R)$ is negative. Hence as R increases for fixed T, $f_T(R)$ increases, reaches a maximum, then decreases. Accordingly, eq. (5) may give two equilibrium radii, the larger corresponding to unstable equilibrium, or one equilibrium radius which is stable against collapse but unstable for growth, or it may afford no equilibrium radius. Inasmuch as $p_{eq}(T)$ is an increasing function of T, $f_T(R)$ is a decreasing function of T for any fixed R, so that the curves of $f_T(R)$ on an $f - R$ diagram form a nonintersecting family, except for the common point at the origin, and the curves for large T fall below those for small T. In particular, the maximum of $f_T(R)$, which occurs when the liquid is heated above its boiling point at the external pressure p_∞, decreases with an increase of T. A typical $f - R$ diagram, drawn for water at 1 atm. external pressure, has been presented in Fig. 1 to illustrate these general remarks.

Consider a gas nucleated bubble which is in stable equilibrium in a liquid below its boiling point, and suppose the temperature to rise slowly. The bubble radius will then increase steadily, with the bubble remaining in stable equilibrium as the temperature increases past the boiling point, until there is finally reached a critical temperature, and a corresponding critical radius, above which the bubble cannot exist in stable equilibrium. A further increase in temperature releases the bubble for dynamic growth.

The nucleation process described can be understood on the basis of the $f - R$ diagram of Fig. 1. The locus of the process for any given bubble is a horizontal line, whose ordinate is fixed by the gas content of the bubble. At the beginning of the process, the bubble is represented by the intersection of the given horizontal line with the $f_T(R)$ curve for the initial temperature. As the temperature increases, the point representing the bubble shifts to the right on the $f - R$ diagram to $f_T(R)$ curves drawn for higher temperatures, and correspondingly the bubble radius increases. The process terminates when the bubble point reaches the $f_T(R)$ curve which has a maximum at the ordinate of the horizontal line. (The locus

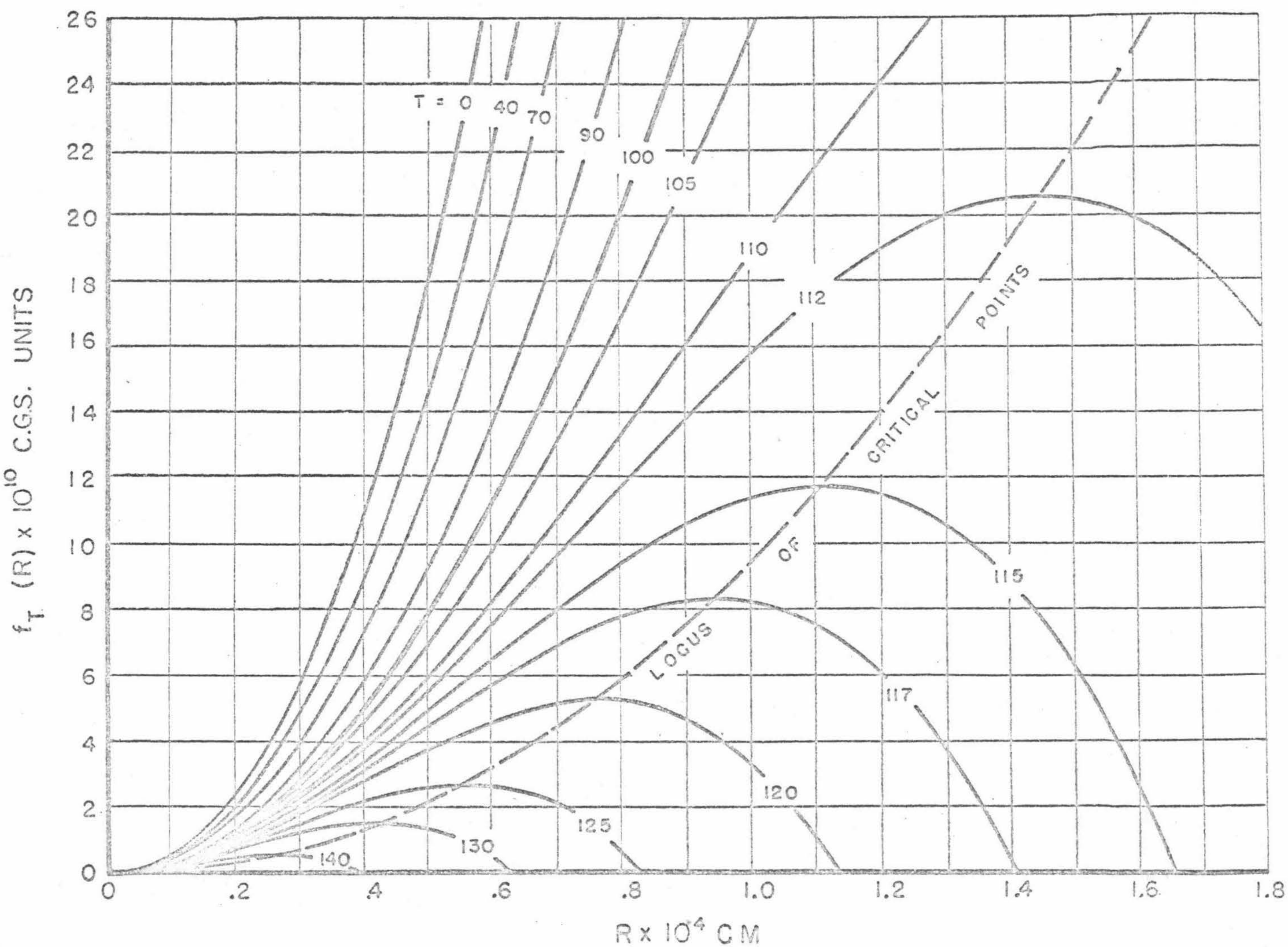

Fig. 1 - f-R diagram for water at 1 atm. external pressure.

of maxima is represented in the diagram by a dashed line, the "locus of critical points".) The bubble considered is then stable against collapse at the temperature of this critical $f_T(R)$ curve and at the radius R_c of its maximum point, but is in a situation of unstable equilibrium with respect to growth. A further increase in temperature upsets the equilibrium and releases the bubble for dynamic growth. Since the surface tension effects relax with an increase of bubble radius, the bubble (which is now in superheated liquid) will continue to grow indefinitely.

The nucleation process is qualitatively similar, but from an analytic standpoint more complex, when the cavitation bubble grows from a solid particle in the liquid, or from a gas pocket stabilized on a solid particle. The bubble may pass through several intermediate stable or unstable equilibria, depending on the size and shape of the particle. Since a pure gas bubble will eventually rise because of gravitational effects and so be removed from the liquid as a source of nucleation, the majority of cavitation bubbles may be supposed to grow from nuclei containing solid particles.

The mechanism discussed above for the release of a cavitation bubble for dynamic growth is the counterpart of boiling. One may analyze in a similar manner the shift of a bubble from stable to unstable equilibrium, and its release for growth, by a decrease in the external pressure. An equivalent process occurs in cavitating liquid flow, the pressure drop in the vicinity of the bubble nucleus being caused by a change in the flow pattern due to the presence of a submerged obstacle. In this case, however, the bubble does not ordinarily continue to grow, but is forced to collapse by a pressure rise which follows along the path of the bubble.*

A different phase of the nucleation problem has been investigated by Glaser,[5,6] who used degassed diethyl ether at 1 atm., superheated 100°C above its normal boiling point of 34°C, as the working fluid in a Bubble Chamber designed to locate the path of a charged atomic particle. A series of

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* Considerable local pressures can develop at the point of bubble collapse. If the bubble collapses near the surface of a submerged object, the sudden unbalance of pressure resulting may be sufficient to dislodge particles from the surface. For a recent study of cavitation damage, see M.S. Plesset and A. Ellis, Proceedings, Annual Meeting ASME, December 1954.

vapor bubbles appears along the track of such a particle in the liquid. If photographed a few microseconds after the detection of the particle, the track is fairly well defined by the bubbles. The physical mechanism of the bubble nucleation in the Bubble Chamber has not, as yet, been fully explained.

In treating the problem of bubble growth, it becomes necessary to make some assumption concerning the nucleation process. The simplest assumption to make about the bubble, and the one which will be made in the analysis to follow, is that the bubble contains initially no permanent gas or solid particle nucleus. It, of course, follows from this assumption $(N = 0)$ and eqs. (4) and (5) above that there is no radius of stable equilibrium for such a bubble. Nevertheless, if the liquid is heated above its boiling point there will still be a radius R_o of unstable equilibrium, which satisfies the equation

$$f_T(R_o) = 0. \tag{7}$$

The radius R_o of the pure vapor bubble given by eq. (7) is related to the critical radius R_c for unstable equilibrium of a gas filled bubble at the same superheat by

$$R_o = \frac{3}{2} R_c. \tag{8}$$

While it is not possible, physically, to form a pure vapor bubble at the radius R_o, the details of growth of such a conceptual bubble differ in no essential way from those of a gas filled bubble growing from unstable equilibrium, or from those of a bubble otherwise nucleated. Equilibrium bubble radii for a pure vapor bubble in water at 1 atm. external pressure, as a function of the water temperature, will be found in Table II (p.65) The equilibrium radius of the pure vapor bubble and the corresponding critical radius of the gas nucleated bubble are decreasing functions of temperature (see Fig. 1).

The method considered in the analysis below for the release of an equilibrium vapor bubble for growth will be an increase of liquid temperature, rather than a decrease of pressure. One reason for this choice is that the temperature change involved in the heating of a liquid usually proceeds at a sufficiently low rate that it ceases to influence the behavior of a bubble soon after the growth of the bubble has begun. The bubble growth then becomes self-determined, or "free". When the bubble growth is initiated by pressure changes, this may not be the case.

Another reason for the choice is the availability of experimental data for the growth of cavitation bubbles in superheated water, with which the predictions of the theory developed below may be compared (see Figs. 4, 5, 6). After the growth of a cavitation bubble has begun, the details of nucleation become unimportant. The bubble tends to become spherical, and is adequately represented by the pure vapor bubble model used here.

The process of growth of a cavitation bubble in a superheated liquid may be described as follows: When the bubble is at its critical radius (R_c for a gas nucleated bubble, the radius R_o of eq. (7) for a pure vapor bubble), it is unstable against expansion, and a slight temperature increase will start the bubble growing. The initial phase of growth is characterized by the relaxation of the effective pressure due to surface tension with an increase of bubble radius. The pressure unbalance causing the bubble growth is thereby increased, and correspondingly the rate of expansion increases rapidly. In order for the bubble to grow, however, evaporation must take place at the bubble wall. Because of the latent heat requirement of evaporation, this requires the temperature at the bubble wall to drop below that of the bulk liquid, which in turn decreases the vapor pressure at the bubble surface. Whether or not the decrease in pressure causes the velocity of the bubble wall eventually to decrease depends upon the rate of increase of bubble surface area. It will be shown that such an effect occurs. The bubble radius ultimately becomes proportional to the square root of the time of growth. In this asymptotic range of bubble expansion, the temperature at the bubble wall approaches the boiling point of the liquid at the external pressure, and the pressure difference producing the bubble growth tends to zero with the radial velocity of the bubble wall.

If the bubble growth is arrested and the bubble forced to collapse by a sudden increase in the exterior pressure, the flow of vapor and the flow of heat at the bubble wall are reversed. Condensation of vapor at the surface of the bubble raises the temperature there, resulting in an increase of vapor pressure which tends to slow down the rate of collapse.

It is thus apparent that coupled with the dynamic problem there is a problem of heat transfer between the liquid and vapor which arises when the bubble changes size. The heat problem will be solved approximately under the assumption that significant heat transfer occurs in the liquid only in a thin shell surrounding the bubble wall. The solution is presented in section III, along with an estimate for the first order correction. The assumption of a thin thermal boundary layer in the liquid is reasonable if the thermal diffusivity of the liquid is sufficiently low.

Insofar as the liquid is concerned, the bubble grows or collapses because of pressure variations at the bubble wall, and possibly at the external surface of the liquid, which set the liquid in motion. Thus the heat transfer problem involves convection effects. A treatment of the heat transfer problem which neglects convection has been given by Forster and Zuber,[7] who use the model of a stationary liquid containing a moving heat source (corresponding to the moving bubble wall). The diffusion solution for the heat problem obtained from this model leads to unrealistic predictions for the rate of bubble growth. An analysis of the diffusion solution is also presented in section III.

The dynamic problems considered here are the growth from unstable equilibrium of a pure vapor bubble in a superheated liquid, and the collapse of a vapor bubble in a liquid below its boiling point. The bubble which collapses is taken to be at rest initially, and in this respect is a model for a cavitation bubble whose growth has been arrested by an increase in the external pressure on the liquid. The model used differs from an actual cavitation bubble in that the liquid temperature is assumed to be uniform when the collapse starts. The temperature field in the liquid for an actual bubble depends on the past history of the bubble, and if non-uniform will affect the initial period of bubble collapse. The solutions for the growth and collapse of vapor bubbles are presented in section IV, together with experimental verification for the case of bubble growth in superheated water.

For the quantitative solution of the heat problem and the dynamic problem, several simplifying physical assumptions have been made. The arguments for the validity of the general assumptions are justified, as they appear in the text, for the case of cavitation bubbles in water. Two basic assumptions may be mentioned here, however; these are that the motion possesses spherical symmetry, and that the motion is irrotational. The latter assumption is independent of the former since, for example, it is possible for a swirling, eddy type of motion to occur within the vapor of a spherical cavitation bubble. The experimental evidence indicates that such motion, if it occurs, does not influence the bubble behavior. The assumption of spherical symmetry is more serious. This requires in principle that the asymmetric effect of gravity upon the bubble behavior be ignored. Actually, the rise of a vapor bubble against gravity is extremely slow, so long as the bubble is small. Thus, for water superheated by about $2^{\circ}C$, no great error is introduced by the buoyant force provided the bubble growth is not followed beyond a radius of the order of 10^{-1} cm, which is much greater than the equilibrium radius of about 1.5×10^{-3} cm for the 102° vapor bubble in water. Bubbles released at higher superheats grow appreciably faster than the 102° bubble, and so are relatively much larger before gravitational effects become important. The collapsing bubble has, effectively, no time to rise against gravity before its collapse is completed.

The emphasis in the following treatment is laid upon the physical, rather than the mathematical aspect of the problem. Thus, a complete table of the integrals appearing in the text has not been given, although a few of the more obscure integrals are evaluated in the Appendix. From a mathematical standpoint, however, it is felt that the equation for the growth of a vapor bubble in a superheated liquid may be of some interest, inasmuch as it offers a tractable example of a nonlinear, integro-differential equation.

II. FORMULATION OF THE PROBLEM

Basic Equations.

In terms of the fluid density, ρ, the (vector) fluid velocity $\underline{v}$, the temperature T, the pressure p, the internal energy e per unit mass of fluid, the stress tensor P, the thermal conductivity k, the coefficient of viscosity η, the time t, and the heat $\dot{q}$ generated per second, per unit volume in the fluid by absorbed radiation, the fundamental Eulerian equations which describe the behavior of a fluid (liquid or vapor) are:

The equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underline{v} = 0. \tag{1}$$

The equation of motion (with the neglect of external body forces, such as gravity)

$$\rho \frac{d\underline{v}}{dt} = \nabla \cdot P. \tag{2}$$

The heat equation

$$\rho \frac{de}{dt} = P : \nabla\underline{v} + \nabla \cdot k\nabla T + \dot{q}. \tag{3}$$

The thermal and caloric equations of state

$$\rho = \rho(p, T), \qquad e = e(p, T). \tag{4}$$

For a Newtonian fluid, the stress tensor is given by*

$$P = -pI + \eta\,[\nabla\underline{v} + (\nabla\underline{v})' - \tfrac{2}{3} I(\nabla \cdot \underline{v})]. \tag{5}$$

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* The notation used here is essentially that of Gibbs, with ∇ denoting the gradient operator. The symbol $\nabla \cdot$ denotes the divergence, $\nabla \times$ the curl, and in the case of the rate of strain tensor $\nabla\underline{v}$ is the vector gradient (a dyadic). The term $P : \nabla\underline{v}$ in (3) represents the trace of the product of the stress and rate of strain tensors. The term $(\nabla\underline{v})'$ in eq. (5) is the transpose of $\nabla\underline{v}$.

For the definition of the stress tensor and a derivation of eqs. (1), (2), (3), see Milne-Thomson, Theoretical Hydrodynamics (Macmillan and Co., Ltd., London, 1949).

In these equations, $\frac{d}{dt}$ denotes the total derivative with respect to time, as computed in a reference frame at rest in the fluid element under consideration;* thus,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \underline{v} \cdot \nabla. \tag{6}$$

Physically, eq. (1) expresses the conservation of mass. Eq. (2) relates the inertial reaction of the given elementary fluid mass to the surface stresses acting upon it (in the absence of external forces). Eq. (3) is essentially the statement of the first law of thermodynamics, relating the increase of internal energy of the mass element to the work done on it by its surroundings in changing its shape and size, the heat energy conducted into it across its surface, and the heat generated in it by absorbed radiation.

By the use of standard vector and tensor identities, the terms in (2) and (3) involving the stress tensor defined by eq. (5) can be reduced to the forms

$$\left.\begin{aligned}
\nabla \cdot P &= -\nabla p + \eta\,[\tfrac{4}{3}\,\nabla(\nabla \cdot \underline{v}) - \nabla\times(\nabla \times \underline{v})], \\
P:\nabla\underline{v} &= -p(\nabla \cdot \underline{v}) + \eta\,\Big\{(\nabla \times \underline{v})^2 + \tfrac{4}{3}\,(\nabla \cdot \underline{v})^2 \\
&\quad + 2\nabla \cdot [\tfrac{1}{2}\,\nabla v^2 - \underline{v} \times (\nabla \times \underline{v}) - \underline{v}(\nabla \cdot \underline{v})]\Big\},
\end{aligned}\right\} \tag{7}$$

provided the coefficient of viscosity η is considered to be constant. Because of the smallness of the coefficient of viscosity of water and its vapor, viscosity effects are not expected to play an important role in the behavior of water vapor bubbles, and will ultimately be ignored. The viscosity terms have been retained, however, so that order of magnitude estimates of their importance may be made.

When the assumption is made that the fluid flow is irrotational

$$\nabla \times \underline{v} = 0 \tag{8}$$

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* Other symbols for the total (substantial, convective, particle) derivative include D/Dt, and a dot placed above the differentiated term: $\dot{q}$.

the forms (7) further reduce to

$$\left.\begin{aligned} \nabla \cdot P &= -\nabla p + \tfrac{4}{3}\eta\, \nabla(\nabla \cdot \underline{v}), \\ P : \nabla\underline{v} &= -p(\nabla \cdot \underline{v}) + \eta \left\{\nabla^2 v^2 - \tfrac{2}{3}(\nabla \cdot \underline{v})^2 - 2\underline{v} \cdot \nabla(\nabla \cdot \underline{v})\right\}. \end{aligned}\right\} \quad (9)$$

If the further assumption is made, in the case of the liquid, of incompressibility (ρ = constant), eq. (1) gives

$$\nabla \cdot \underline{v} = 0, \quad (10)$$

and eqs. (9) become simply

$$\left.\begin{aligned} \nabla \cdot P &= -\nabla p, \\ P : \nabla\underline{v} &= \eta \nabla^2 v^2. \end{aligned}\right\} \quad (11)$$

It will be observed, on substituting eq. (11) into eq. (2), that the viscosity terms disappear completely from the equation of motion for the case of irrotational motion of an incompressible fluid. If the fluid is viscous, the motion may still be influenced by viscous heat generation, however, provided significant heat transfer effects take place.

<u>The Problem in the Liquid</u>.

It follows from the assumption that the liquid motion is irrotational (eq. (8)) that there exists a velocity potential ϕ throughout the liquid, such that

$$\underline{v} = -\nabla\phi. \quad (12)$$

Since, further, the liquid is taken to be incompressible (eq. (10)), the velocity potential is a solution of Laplace's equation

$$\nabla^2 \phi = 0. \quad (13)$$

The spherically symmetric solution of eq. (13) is of the form

$$\phi = \frac{A(t)}{r} + B(t), \quad (14)$$

where r is the radial coordinate from the center of the bubble. The liquid velocity corresponding to eq. (14) is purely radial, and given by eq. (12) as

$$v = \frac{A(t)}{r^2} . \tag{15}$$

If the liquid velocity at the bubble wall is denoted by $v(R)$,* eq. (15) gives the relation

$$A(t) = R^2(t)\, v(R), \tag{16}$$

where $R(t)$ is the radius of the bubble surface. Eq. (15) thus becomes

$$v(r,t) = \frac{R^2(t)}{r^2}\, v(R), \tag{17}$$

and if the velocity potential is normalized to zero at $r = \infty$, eq. (14) becomes

$$\phi(r,t) = \frac{R^2(t)\, v(R)}{r} . \tag{18}$$

The equation of motion, according to eqs. (2), (11), is

$$\rho\left[\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v}\right] = -\nabla p. \tag{19}$$

The vector identity

$$\underline{v} \times (\nabla \times \underline{v}) = \frac{1}{2} \nabla v^2 - \underline{v} \cdot \nabla \underline{v}$$

and the assumption $\nabla \times \underline{v} = 0$ give

$$\underline{v} \cdot \nabla \underline{v} = \frac{1}{2} \nabla v^2;$$

hence, by eq. (12), the equation of motion (19) may be written

$$\rho \nabla\left[- \frac{\partial \phi}{\partial t} + \frac{1}{2} v^2\right] = -\nabla p,$$

from which a Bernoulli relation

$$- \frac{\partial \phi}{\partial t} + \frac{1}{2} v^2 = - \frac{p}{\rho} + C(t) \tag{20}$$

follows by integration, the density having been taken constant. From eqs. (17),

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* $v(R)$ is, in general, not exactly equal to the radial velocity $\dot{R}$ of the bubble wall (because of evaporation or condensation occurring there.)

(18), the left side of eq. (20) vanishes at $r = \infty$, so that $C(t)$ in eq. (20) is simply the external pressure p_∞ divided by the liquid density:

$$C(t) = \frac{p_\infty}{\rho} .$$

Eq. (20) thus becomes

$$\frac{\partial \phi}{\partial t} - \frac{1}{2} v^2 = \frac{p(r,t) - p_\infty}{\rho} . \tag{21}$$

Because the density of the liquid is assumed constant, the internal energy e can be a function only of the temperature T. Over the limited range of temperatures which will be considered here, the internal energy may be considered to vary linearly with the temperature. On neglecting any constant internal energies, the caloric equation of state therefore reduces to

$$e = c_v T, \tag{22}$$

where c_v is the specific heat (at constant volume) of the liquid. The thermal conductivity k, like the specific heat, will be taken constant over the temperature ranges considered. Eqs. (3), (11), and (22) thus combine to give for the internal energy equation of the liquid

$$\rho c_v \left[\frac{\partial T}{\partial t} + v \cdot \nabla T\right] = k\nabla^2 T + \eta \nabla^2 v^2 + \dot{q}. \tag{23}$$

In the analysis to follow, the viscosity term $\eta \nabla^2 v^2$ in eq. (23) will be neglected. By using the solutions thus obtained, it is possible to estimate the contribution of this term to the total rate of heat generation per unit volume of liquid. The specification (17) for v gives

$$\eta \nabla^2 v^2 = 12 \eta \frac{v^2}{r^2} ,$$

and accordingly, the viscous heat generation is a maximum at the bubble wall, where it amounts to

$$12 \eta \frac{v^2(R)}{R^2}$$

per second, per unit volume. Here $v(R)$ represents the velocity of the liquid at the bubble wall, which may be approximated by the radial velocity $\dot{R}$ of the bubble wall itself.* The coefficient of viscosity of water near

* This approximation, which is plausible physically, will be shown to be accurate to about 1 part in 1000.

the boiling point is about 3×10^{-3} c.g.s. units.* The solution for vapor bubble growth to be presented below gives for a bubble growing in water at 1 atm., superheated to 103°C, a maximum radial velocity $\dot{R}_{max} = 32$ cm/sec when the bubble radius is about $R = 3 \times 10^{-3}$ cm (see Fig. 7). Combining these figures, we find for the rate of viscous heat generation at this time time

$$\eta \nabla^2 v^2 \simeq 12\eta \frac{\dot{R}^2_{max}}{R^2} = 4 \times 10^6 \text{ erg/cc}\cdot\text{sec} \simeq 10^{-1} \text{ cal/cc}\cdot\text{sec}.$$

But the total temperature drop at the bubble wall near the time of maximum radial velocity (see Fig. 8) is about 10^4 °C/sec, corresponding to a heat loss from the liquid at the bubble wall at this time of

$$\left|\rho c_v \frac{dT(R)}{dt}\right| \simeq 10^4 \text{ cal/cc}\cdot\text{sec},$$

due essentially to the evaporation occurring there. The viscous heat generation drops off sharply away from the velocity maximum. Clearly, viscosity plays a negligible part in determining the growth of vapor bubbles in water. Eq. (23) will therefore be written for solution as

$$\rho c_v[\frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T] = k\nabla^2 T + \dot{q} \; . \qquad (24)$$

The foregoing development of the equations for the liquid has been based essentially on the assumption that the liquid is incompressible. The validity of this assumption depends upon the ratio of the velocities attained by the liquid to the velocity of sound in the liquid. For the growing vapor bubble, the maximum velocity at the bubble wall is never larger than a few meters per second for the highest superheats considered, so that compressibility effects in the liquid may be safely ignored.

For the case of the collapsing bubble, several of the assumptions made above may fail near the point of collapse, if the solutions are carried that far. Thus, the temperature at the bubble wall, which is initially below the boiling point, rises sharply near the end of collapse, possibly

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* A tabulation of physical constants will be found in Appendix A.

approaching the critical temperature of the liquid. The parameters ρ, k, c_v, etc. of the liquid cannot be taken constant, of course, over such an extreme temperature variation, nor is it valid to consider the liquid incompressible. Perhaps the most significant error in the basic assumptions, for the case of the collapsing bubble, lies in the fact that the spherical shape is inherently unstable near the point of collapse.(8) The collapsing bubble tends (theoretically and experimentally) to shatter before collapse.

For these reasons, although the assumptions made above will be retained, the calculations for the collapsing bubble will be carried only far enough to indicate the trend of behavior of the physical quantities involved.

The Problem in the Vapor.

In the case of the vapor, the main simplifying assumptions are related to the smallness of the vapor density in comparison with that of the liquid. Thus, the physical effects of the vapor inertia may be expected to have a negligible influence on the rate of bubble growth or collapse. It will be shown that the vapor may safely be considered to be in a state of thermal and dynamic equilibrium, insofar as its internal behavior is concerned. To do this, it is sufficient to use order of magnitude estimates.

The equation of motion of the vapor follows from eqs. (2), (8), and (9), and is given by*

$$\rho\left[\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v}\right] = -\nabla p + \frac{4}{3}\eta \nabla(\nabla \cdot \underline{v}). \tag{25}$$

The velocity in the vapor is certainly smaller in magnitude than the velocity of the bubble wall, because of the evaporation which takes place when the bubble grows or the condensation of vapor which occurs when the bubble collapses. The vapor density is smaller than the liquid density in a ratio of about 1:1000, and the coefficient of viscosity of the vapor is smaller in a ratio of roughly 1:10. The pressure gradient in the vapor may therefore be assumed smaller than the gradient in the liquid by at least an order of magnitude. An estimate of the pressure gradient in the liquid may be made

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* The symbols appearing in this part of section II refer to the vapor, unless otherwise indicated.

by again putting the liquid velocity at the bubble wall equal to the bubble wall velocity $\dot{R}$ in eq. (17), and using this to evaluate eq. (19) at the bubble wall. The result for the liquid is simply that

$$\left.\frac{\partial p_{liq}}{\partial r}\right|_{r=R(t)} = -\rho_{liq}\ddot{R},$$

where $\ddot{R}$ is the radial acceleration of the bubble wall. For water at 103°C, the maximum radial acceleration of the bubble wall is about 6×10^5 cm/sec^2 (see Fig. 7), giving for the maximum pressure gradient at the bubble wall 6×10^5 dynes/cm^2/cm, or about .6 atm./cm. The maximum pressure gradient in the vapor is not more than about 1/10 of this, on the basis of the above estimate, and it occurs when the bubble radius is about 2×10^{-3} cm. Thus, the pressure variation in the bubble is at most of the order of 10^{-4} atm. But the pressure itself is of the same order as the external pressure of 1 atm. It is thus clear that the pressure may be taken as uniform within the bubble,

$$p_{vap} = p(t). \tag{26}$$

For order of magnitude purposes it is sufficient to consider the vapor to be thermally and calorically perfect:

$$p = \rho BT, \tag{27}$$

$$e = c_v T, \tag{28}$$

where B in (27), is the universal gas constant divided by the molecular weight of the vapor, and c_v in (28) is the specific heat (at constant volume) of the vapor. The heat equation for the vapor becomes

$$\rho c_v[\frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T] = k\nabla^2 T - p(\nabla \cdot \underline{v})$$

$$+ \eta \left\{\nabla^2 v^2 - \frac{2}{3}(\nabla \cdot \underline{v})^2 - 2v \cdot \nabla(\nabla \cdot \underline{v})\right\} \tag{29}$$

according to eqs. (3) and (9), if the radiant heating in the vapor is ignored. The thermal conductivity, specific heat and viscosity coefficient of the vapor are about an order of magnitude smaller than the corresponding quantities for the liquid. On making the same approximations for the heat equation (29) as for the equation of motion, we obtain an approximate relation

$$k\nabla^2 T = p\nabla \cdot \underline{v},$$

which reduces to

$$\nabla^2(kT + p\phi) = 0 \tag{30}$$

if the velocity potential relation for the velocity and the uniformity of p and k are used. Inasmuch as the pressure, temperature and velocity potential are all finite at the origin, the only solution of (30) consistent with spherical symmetry is of the form

$$kT + p\phi = C(t). \tag{31}$$

The velocity potential remains undetermined to an additive function of time, which can be so chosen that $C(t) = 0$ in (31). Eq. (31) then yields the relation

$$\phi = -\frac{k}{p}\,T, \tag{32}$$

and if the perfect gas law (27) is used in (32) it gives the further relation

$$\phi = -\frac{k}{\rho B}\,. \tag{33}$$

Eq. (33) may now be substituted into the equation of continuity (1), giving

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot\rho\,\underline{v} = \nabla\cdot\rho\,\nabla\phi = \frac{k}{B}\,\nabla\cdot\frac{1}{\rho}\,\nabla\rho,$$

or

$$\rho B\,\frac{\partial\ln\rho}{\partial t} = k\nabla^2\ln\rho\,. \tag{34}$$

Eq. (34) is a diffusion-type equation, which may be compared with the heat equation written for stationary vapor

$$\rho c_v\,\frac{\partial T}{\partial t} = k\nabla^2 T,$$

or

$$\nabla^2 T = \frac{1}{D}\,\frac{\partial T}{\partial t}, \qquad D = \frac{k}{\rho c_v}\,. \tag{35}$$

The function in eq. (34) replacing the thermal diffusivity D of the vapor in eq. (35) is

$$|\phi| = \frac{k}{\rho B}\,. \tag{36}$$

If the vapor molecules may be supposed to have, say, three translational and three rotational degrees of freedom, then $c_v = 3B$. Hence if the vapor were stationary, we should have from (35) and (36)

$$|\phi| \simeq 3D. \tag{37}$$

Eq. (37) will be of the right order of magnitude even if the density varies. Now, the thermal diffusivity D of saturated water vapor at 103°C is about .3 cm²/sec. The characteristic diffusion length for eq. (34) is thus about $\sqrt{4|\phi|t} \approx 2\sqrt{t}$. The significant time for the 103° bubble is about 10^{-4} sec, roughly the time between the end of the relaxation period (when the rate of bubble growth becomes significant) and the time of the velocity maximum (see Fig. 7), giving for the diffusion length $\sqrt{4|\phi|t} \approx .02$ cm, or about six times the bubble radius at the velocity maximum. There is, therefore, an insignificant variation of $\ln \rho$ with position in the bubble, so that the vapor density may be considered a function of time alone,

$$\rho_{vap} = \rho(t). \tag{38}$$

Eqs. (32) and (33) then show that also

$$T_{vap} = T(t), \tag{39}$$

$$\phi_{vap} = \phi(t). \tag{40}$$

It is not legitimate, of course, to argue from eq. (40) that the vapor is at rest, since it is the small terms in ϕ which have already been neglected in arriving at (40) that determine the velocity. This difficulty can be traced to the normalization chosen for ϕ. However, an estimate for the velocity is readily obtained from eq. (38). Consider a sphere of radius r within the vapor. The mass of vapor in such a sphere, by (38), is simply

$$m(r,t) = \frac{4}{3}\pi r^3 \rho(t). \tag{41}$$

If, now, the independent variables in (41) are chosen to be m and t, rather than r and t, eq. (41) may be written in an alternative notation as

$$m = \frac{4}{3}\pi \rho(t)\, r^3(m,t), \tag{42}$$

the change corresponding to the adoption of Lagrangian rather than Eulerian coordinates. Differentiation of (42) with respect to t, holding m fixed, shows that

$$r \frac{\partial \rho}{\partial t} + 3 \rho \frac{\partial r}{\partial t} = 0,$$

or since $\frac{\partial r}{\partial t}$ is now the vapor velocity, that

$$v_{vap}(r,t) = - \frac{r}{3\rho} \frac{\partial \rho}{\partial t}, \quad = - \frac{r}{3\rho} \frac{d\rho}{dt}. \tag{43}$$

Inasmuch as the origin for r in the above development was arbitrary, eq. (43) implies a uniform dilation or contraction of the vapor within the bubble, which is consistent with the uniformity at ρ. Eq. (43) indicates a radial velocity in the vapor at the bubble wall of about .4 cm/sec for the 103° bubble when the velocity of the bubble wall reaches its maximum of about 32 cm/sec.

In the discussion of the growing vapor bubble in a superheated liquid, effects related to the velocity of the vapor will be neglected, thus incurring an error of a few per cent in the results. In the discussion of the collapsing bubble, the large temperature variations at the bubble wall may be expected to cause significant changes in the vapor density, and so the effects of the vapor velocity will be included.

It may be noted in passing that for a uniform (irrotational) dilation or contraction of the vapor, such as is indicated by eqs. (38) or (43), the viscosity terms in the heat equation (29) vanish identically.

Boundary Conditions.

If the terms involving viscosity are omitted from the basic equations (1), (2), (3) and the equations of state are substituted in, the resulting equations are of first differential order in $\underline{v}$ and p, and second order in T. In order to match solutions for the liquid and vapor across the bubble wall, relations must therefore be provided connecting the values of $\underline{v}$ and p, and the value and normal derivative of T across the interface. Because of the assumption of spherical symmetry, no further relations are needed if the viscosity terms are retained.

Consider a differential cone Γ extending from the center of the vapor bubble (the origin) to a point indefinitely far away in the liquid, whose generators are straight lines through the origin, and whose differential cross section at the bubble wall is Σ. In this cone, mass is conserved

$$\frac{d}{dt}\int_\Gamma \rho d\tau + \oint_\Gamma \underline{n} \cdot \rho \underline{v}\, dS = 0. \tag{44}$$

The equation of motion of the cone is*

$$\frac{d}{dt}\int_\Gamma \rho \underline{v}\, d\tau + \oint_\Gamma \underline{n} \cdot \rho \underline{vv}\, dS = \oint_\Gamma \underline{n} \cdot P\, dS - \int_\Sigma \frac{2\sigma}{R}\, \underline{n}\, dS, \tag{45}$$

and the energy balance equation is

$$\frac{d}{dt}\left\{\int_\Gamma \rho(e + \tfrac{1}{2} v^2) d\tau + \int_\Sigma \sigma\, dS\right\} + \oint_\Gamma \underline{n} \cdot \rho \underline{v}(e + \tfrac{1}{2} v^2)\, dS$$

$$= \int_\Gamma \dot{q}\, d\tau + \oint_\Gamma \underline{n} \cdot (P \cdot \underline{v} + k\nabla T)\, dS. \tag{46}$$

In these equations, $\underline{n}$ denotes the outward drawn normal to the cone in $\oint_\Gamma dS$, and the unit normal to Σ extending away from the origin in $\int_\Sigma dS$. The surface integrals on the left side of the equations represent transport terms; these must be added because the elements of integration do not move with the fluid. To evaluate the integrals we shall need the differential equations, which may be written

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underline{v} = 0, \tag{47}$$

$$\frac{\partial \rho \underline{v}}{\partial t} + \nabla \cdot [\rho \underline{vv} - P] = 0, \tag{48}$$

$$\frac{\partial}{\partial t}[\rho(e + \tfrac{1}{2} v^2)] + \nabla \cdot [\rho \underline{v}(e + \tfrac{1}{2} v^2) - P \cdot \underline{v} - k\nabla T] = \dot{q}, \tag{49}$$

eq. (49) being a combination of eqs. (2) and (3).

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* Since the stress tensor does not account for the molecular forces responsible for surface tension, the force due to surface tensions must be written explicitly into eq. (45), and the corresponding surface energy into eq. (46). For a classical treatment of the theory of surface tension, see Joos, Theoretical Physics (Hafner Publishing Co., Inc., New York, 1934), Chapt. IX, section 8.

The equations (47), (48), (49) are all of the form

$$\frac{\partial a}{\partial t} + \nabla \cdot b = c, \tag{50}$$

a, b and c being suitable scalars, vectors or tensors. The integral relations require a knowledge of

$$\frac{d}{dt} \int_\Gamma a d\tau .$$

The change in the integral $\int_\Gamma a d\tau$ during a time dt is

$$d \int_\Gamma a d\tau = \int_{r<R+\dot{R}dt} \left[a' + \frac{\partial a'}{\partial t} dt \right] d\tau - \int_{r<R} a' d\tau$$

$$+ \int_{r>R+\dot{R}dt} \left[a + \frac{\partial a}{\partial t} dt \right] d\tau - \int_{r>R} a d\tau, \tag{51}$$

where a' is the value of a written for the vapor. The volume element $d\tau$ is here considered fixed in space. To first order in dt, (51) is

$$d \int_\Gamma a d\tau = \int_{R<r<R+\dot{R}dt} (a' - a) d\tau + dt\left[\int_{r<R} \frac{\partial a'}{\partial t} d\tau + \int_{r>R} \frac{\partial a}{\partial t} d\tau \right].$$

This may be transformed with the aid of the relation (50) and the divergence theorem, to

$$\frac{d}{dt} \int_\Gamma a d\tau = \int_{r=R} \dot{R}(a' - a) dS + \int_{r<R} c' d\tau - \oint_{r<R} \underline{n} \cdot b' dS$$

$$+ \int_{r>R} c d\tau - \oint_{r>R} \underline{n} \cdot b dS$$

$$= \int_\Sigma \dot{R}(a' - a) dS + \int_\Gamma c d\tau - \oint_\Gamma \underline{n} \cdot b dS - \int_\Sigma \underline{n} \cdot (b' - b) dS$$

$$= \Sigma \cdot [\dot{R}(a' - a) - \underline{n} \cdot (b' - b)]_\Sigma - \oint_\Gamma \underline{n} \cdot b dS + \int_\Gamma c d\tau . \tag{52}$$

Applying (52) to eqs. (44)-(49), one obtains in a straightforward fashion

$$\left.\begin{aligned}
&[\dot{R}(\rho' - \rho) - \underline{n} \cdot (\rho'\underline{v}' - \rho\underline{v})]_{\Sigma} = 0, \\
&[\dot{R}(\rho'\underline{v}' - \rho\underline{v}) - \underline{n} \cdot (\rho'\underline{v}'\underline{v}' - \rho\underline{vv} - P' + P)]_{\Sigma'} = -\frac{2\sigma}{R}\underline{n}_{\Sigma}, \\
&-\frac{2\sigma}{R}\dot{R} = \Big\{ \dot{R}[\rho'(e + \tfrac{1}{2}v'^2) - \rho(e + \tfrac{1}{2}v^2)] \\
&\qquad - \underline{n} \cdot [\rho'\underline{v}'(e' + \tfrac{1}{2}v'^2) - \rho\underline{v}(e + \tfrac{1}{2}v^2) - P' \cdot v' \\
&\qquad\qquad + P \cdot \underline{v} - k'\nabla T' + k\nabla T]\Big\}_{\Sigma}.
\end{aligned}\right\} \tag{53}$$

Because of the spherical symmetry,

$$\underline{n} \cdot P = \underline{n}[-p + \frac{4}{3}\eta(\frac{\partial v}{\partial r} - \frac{v}{r})] \tag{54}$$

on Σ (the same relation holding for P'). The use of (54) in (53) leads to the results

$$\rho(\dot{R} - v) = \rho'(\dot{R} - v'), \tag{55}$$

$$p + \frac{2\sigma}{R} = p' + (v - v')\rho'(\mathring{R} - v') + \frac{4}{3}\eta(\frac{\partial v}{\partial r} - \frac{v}{r}) - \frac{4}{3}\eta'(\frac{\partial v'}{\partial r} - \frac{v'}{r}), \tag{56}$$

$$\begin{aligned}
k\frac{\partial T}{\partial r} - k'\frac{\partial T'}{\partial r} = \rho'(\dot{R} - v')[L + \tfrac{1}{2}(\dot{R} - v')^2 - \tfrac{1}{2}(\dot{R} - v)^2 \\
- \frac{4}{3}\frac{\eta'}{\rho'}(\frac{\partial v'}{\partial r} - \frac{\partial v}{\partial r}) + \frac{4}{3}\frac{\eta}{\rho}(\frac{\partial v}{\partial r} - \frac{v}{r})]
\end{aligned} \tag{57}$$

at $r = R$, where in (57) we have put

$$L = e' - e + \frac{p'}{\rho'} - \frac{p}{\rho}; \tag{58}$$

according to the first law of thermodynamics, L is the latent heat of evaporation at the bubble wall. Evidently, eq. (55) expresses the conservation of momentum at the bubble wall. The last terms in (57), (58) represent kinematic (mass transfer) and viscous corrections to the vapor pressure and heat transfer relations holding at the bubble wall.

There is, finally, the condition of temperature continuity across the bubble surface

$$T' = T. \tag{59}$$

A temperature discontinuity would imply an infinite heat conduction through the surface.

The momentum condition (55), which may be written

$$v = \dot{R}[1 - \frac{\rho'}{\rho}(1 - \frac{v'}{\dot{R}})], \tag{60}$$

shows that the liquid velocity at the bubble wall can differ from the bubble wall velocity by at most terms of relative order $\rho'/\rho \approx 1/1000$. For all practical purposes, (55) may therefore be replaced by

$$v_{liq}(R) = \dot{R}. \tag{61}$$

As has been mentioned previously, the vapor velocity is small in comparison with the bubble wall velocity. The momentum transport correction in eq,(56) is thus approximately $\rho'\dot{R}^2$. For this to compare with p', which is about 1 atm $\approx 10^6$ c.g.s units, $\dot{R}$ must equal about 300 m/sec, i.e. be comparable with sonic velocity in the vapor. Such large velocities will not be considered here, so that the momentum transport correction in eq. (56) may be neglected. Similarly, the kinetic energy transport corrections to the heat transfer relation (57) are completely negligible in comparison with the latent heat of evaporation. (For water, $L \approx 2 \times 10^{10}$ erg/gm.)

The viscosity corrections in (56), (57) may be evaluated by eqs. (17), (43), (60). The contribution of the vapor vanishes identically. The contribution of the liquid amounts to

$$\frac{4}{3}\eta\left(\frac{\partial v}{\partial r} - \frac{v}{r}\right)_R = -4\eta\frac{v}{r}\Big|_R = -4\eta\frac{\dot{R}}{R}$$

in eq. (56), and this divided by ρ in eq. (57). The net effect of viscosity is thus to increase the surface tension σ in (56) by $2\eta\dot{R}$, and to decrease the latent heat L in (57) by $4\eta\dot{R}/\rho R$. For a vapor bubble growing in water, the latter correction is entirely negligible. The surface tension increase amounts to .2 and .9 dynes/cm at the time of the velocity maximum of the 103° and 106° bubbles, respectively (see Figs. 7,9). This is of the order of the thermal variation in σ, which has already been neglected. For the collapsing bubble, these viscous effects become important only near the point of collapse.

With the neglect of the kinematic and viscous corrections, the pressure relation (56) reduces to

$$p_{vap} = p_{liq} + \frac{2\sigma}{R}. \tag{62}$$

Since the temperature within the vapor is considered to be uniform, the heat transfer relation (57) reduces to

$$k\frac{\partial T}{\partial r} = L\rho'(\dot{R} - v').$$

By eq. (43), this may also be written

$$R^2\left(k \frac{\partial T}{\partial r}\right)_{liq} = \frac{L}{3} \frac{d}{dt} (R^3 \rho_{vap}). \tag{63}$$

When the vapor is at rest relative to the interface, the quantities p_{vap} and ρ_{vap} are equal to the equilibrium vapor pressure and density p_{eq} and ρ_{eq} of the liquid at the temperature of the bubble surface. But when a relative velocity exists they will differ, by an amount depending on the nature of the liquid. A relation connecting these which holds when the vapor may be considered a perfect gas in a state of complete equilibrium ($v_{vap} = 0$) has been given by Mathews,[9] on the basis of previous work by Plesset.[10] In the notation used here, Mathews' relation is

$$\frac{p_{vap}}{p_{eq}} = \frac{\rho_{vap}}{\rho_{eq}} = \frac{\bar{c}}{\bar{c} + \dot{R}}, \tag{64}$$

where $\bar{c}$ is a characteristic velocity, related to the velocity of sound c in the vapor and the specific heat ratio γ of the vapor by

$$\bar{c} = \frac{\alpha}{\sqrt{2\pi\gamma}} c. \tag{65}$$

The parameter α appearing in (65) is called the "accomodation coefficient" of the liquid, and measures the fraction of the surface available for evaporation or condensation. For non-polar liquids α is near unity, but for polar liquids with hydrogen bonding α may be appreciably smaller. For a water surface near $10^\circ C$, α is reported by Wyllie[11] to have the value .04. This experimental value was obtained by measuring the time required for a sample of liquid to evaporate into a partial vacuum. Due to experimental difficulties, the value of α for water has not been measured at higher temperatures.

If the value $\alpha = .04$ and the values $\gamma = 1.33$, $c = 5 \times 10^4$ cm/sec are used in (65), they give for the characteristic velocity of water $\bar{c} \approx 7$ m/sec. Correspondingly, one might expect a significant deficiency in vapor pressure and density to occur when a vapor bubble is growing in water at only a moderate rate. The situation in the case of a collapsing bubble is even more critical. The large pressures developed within the collapsing bubble because of the inaccesibility of the bubble surface for condensation would severely limit the rate of collapse, and might be expected to result in the appearance of condensation throughout the vapor.

These conclusions, however, do not appear to be borne out by experiment. Thus, the pressure-limited collapse described does not occur (radial velocities of collapse in water which are certainly in excess of 25 m/sec have been reported by Ellis[12]), and condensation has not been observed to occur within collapsing cavitation bubbles, except possibly near the point of collapse. These facts indicate that the value of α for water at even 10°C may be much greater than .04, and possibly point to a significant increase of α with an increase of temperature.*

We shall therefore assume the velocity $\bar{c}$ in eq. (64) to be sufficiently large that vapor pressure and density discrepancies may be ignored, so that we may take

$$p_{vap} = p_{eq}, \qquad \rho_{vap} = \rho_{eq} \tag{66}$$

at the bubble wall.

Conclusion.

From eqs. (17), (61), eq. (21) becomes

$$p_{liq}(r,t) = p_\infty + \rho_{liq}\left[\frac{R^2\ddot{R} + 2R\dot{R}^2}{r} - \frac{1}{2}\,\frac{R^4\,\dot{R}^2}{r^4}\right]. \tag{67}$$

Since $p_{liq}(R) = p_{eq}(T) - \frac{2\sigma}{R}$ by eqs. (62), (66), eq. (67) becomes at the bubble wall

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{p_{eq}(T) - p_\infty}{\rho_{liq}} - \frac{2\sigma}{\rho_{liq}R}, \tag{68}$$

an equation of motion for the radius R of the bubble wall. Eq. (68) was given by Plesset.[13] $p_{eq}(T)$ in (68) refers to the equilibrium vapor pressure of the liquid at the temperature of the bubble wall.**

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* It is not the experimental value of α which is questioned here, but the determination of the temperature at the surface of evaporation. In the case of water, the rate of evaporation is large, and a steep temperature gradient develops at the surface (possibly reaching 10^2 or 10^3 °C/cm).

** As indicated previously in the discussion, eq. (68) may be considered valid so long as $\dot{R}$ remains small in comparison with the sonic velocity in the liquid. A correction to the equation of motion (68) which takes the compressibility of the liquid into account (up to terms quadratic in $\dot{R}/c_{liq}$) has been given by F.R. Gilmore (HDLCIT Report 26-4, April 1952) on the basis of the Kirkwood-Bethe hypothesis.

Coupled with eq. (68) is the heat equation for the liquid, eq. (24):

$$\rho c_v[\frac{\partial T}{\partial t} + v \cdot \nabla T] = k\nabla^2 T + \dot{q}, \tag{69}$$

with the boundary condition

$$R^2 k \left.\frac{\partial T}{\partial r}\right|_{r=R(t)} = \frac{L}{3} \frac{d}{dt} (R^3 \rho_{eq}(T)) \tag{70}$$

(eqs. (63), (66)). $\rho_{eq}(T)$ in (70) is the equilibrium vapor density of the liquid at the temperature of the bubble wall. It will be assumed that initially the temperature in the liquid is uniform

$$T(r,0) = T_o. \tag{71}$$

Together with the initial conditions for eq. (68), eqs. (68)-(71) determine the problem of vapor bubble behavior.

III. THE HEAT PROBLEM

The system of equations II (69), (70), (71) which define the heat transfer problem in the liquid may be written

$$\left.\begin{aligned} \nabla^2 T &= \frac{1}{D}\left[\frac{\partial T}{\partial t} + \underline{v}\cdot\nabla T\right] - \frac{1}{k}\,\dot{q}(t), \\ \left.\frac{\partial T}{\partial r}\right|_{r=R(t)} &= R^2\,F(t), \\ T(r,0) &= T_o, \end{aligned}\right\} \qquad (1)$$

where $D = \dfrac{k}{\rho c_v}$ and

$$\left.\begin{aligned} v &= \frac{R^2\,\dot{R}}{r^2}, \\ F(t) &= \frac{L}{3k}\,\frac{1}{R^4}\,\frac{d}{dt}\left[R^3\rho_{eq}(T)\right]. \end{aligned}\right\} \qquad (2)$$

At $r = \infty$ the temperature in the liquid becomes uniform, so that the first and last of eqs. (1) give on integration

$$T_\infty \equiv T(\infty\,,\,t) = T_o + \frac{D}{k}\,q(t), \qquad (3)$$

if q is chosen so that $q(0) = 0$. To standardize the solution it is desirable to use instead of T the dependent variable

$$\theta = T - T_\infty\,, \qquad (4)$$

which vanishes at $r = \infty$ and satisfies the system

$$\left.\begin{aligned} \nabla^2\theta &= \frac{1}{D}\left[\frac{\partial\theta}{\partial t} + \underline{v}\cdot\nabla\theta\right], \\ \left.\frac{\partial\theta}{\partial r}\right|_{r=R} &= R^2F(t), \\ \theta(r,0) &= \theta(\infty\,,\,t) = 0. \end{aligned}\right\} \qquad (5)$$

Convection Solution.

Because of the boundary condition at the moving bubble wall, it is convenient to transform (5) from Eulerian to Lagrangian coordinates. Coordinates appropriate to the present problem are

$$\left.\begin{aligned} m &= \frac{1}{3}\,[r^3 - R^3(t)], \\ t &= t. \end{aligned}\right\} \qquad (6)$$

The Lagrangian coordinate m measures essentially the mass of liquid contained within a sphere of radius r about the center of the bubble, the liquid density having been assumed constant. In terms of m and t, the system (5) becomes

$$\left.\begin{aligned} \frac{\partial}{\partial m}\,[r^4\,\frac{\partial \theta}{\partial m}] &= \frac{1}{D}\,\frac{\partial \theta}{\partial t}\,, \\ \left.\frac{\partial \theta}{\partial m}\right|_{m=0} &= F(t), \\ \theta(m,0) = \theta(\infty\,,\,t) &= 0. \end{aligned}\right\} \qquad (7)$$

These equations can be put in more tractable form by introducing a temperature potential U, defined by

$$\theta = \frac{\partial U}{\partial m}\,. \qquad (8)$$

The differential equation

$$\frac{\partial}{\partial m}\,[r^4\,\frac{\partial^2 U}{\partial m^2} - \frac{1}{D}\,\frac{\partial U}{\partial t}] = 0$$

may be then integrated once with respect to m to yield

$$r^4\,\frac{\partial^2 U}{\partial m^2} - \frac{1}{D}\,\frac{\partial U}{\partial t} = J(t),$$

where $J(t)$ is an arbitrary function of time. From eq. (8),

$$U = \int_0^m \theta\,dm + K(t),$$

and the function $K(t)$ may be chosen so that $J(t) = 0$, and also so that $U(m,0) = 0$. The system of equations to be solved then reduces to

$$\left.\begin{aligned} & r^4 \frac{\partial^2 U}{\partial m^2} - \frac{1}{D}\frac{\partial U}{\partial t} = 0, \\ & \left.\frac{\partial^2 U}{\partial m^2}\right|_{m=0} = F(t), \\ & U(m,0) = \left.\frac{\partial U}{\partial m}\right|_{m=\infty} = 0. \end{aligned}\right\} \tag{9}$$

The diffusion problem thus defined can be solved by an iterative procedure if the assumption is made that U varies appreciably only near $m = 0$. This is equivalent to the assumption that the temperature variation in the liquid is localized in a thin "thermal boundary layer" surrounding the bubble wall, which is reasonable if (as is the case with water) the thermal diffusivity D of the liquid is sufficiently small. To utilize the assumption, we shall rewrite the differential equation as

$$R^4 \frac{\partial^2 U}{\partial m^2} - \frac{1}{D}\frac{\partial U}{\partial t} = (r^4 - R^4)\frac{\partial^2 U}{\partial m^2}, \tag{10}$$

and treat the right side of (10) as a perturbing heat source. It is convenient to use in (10) a new time variable τ, defined by

$$\tau = \int_0^t R^4(t)\, dt, \tag{11}$$

in terms of which the differential equation becomes

$$\frac{\partial^2 U}{\partial m^2} - \frac{1}{D}\frac{\partial U}{\partial \tau} = \left(\frac{r^4}{R^4} - 1\right)\frac{\partial^2 U}{\partial m^2}.$$

The system for the unperturbed solution U_o is

$$\left.\begin{aligned} & \frac{\partial^2 U_o}{\partial m^2} - \frac{1}{D}\frac{\partial U_o}{\partial \tau} = 0, \\ & \left.\frac{\partial^2 U_o}{\partial m^2}\right|_{m=0} = F(\tau), \\ & U_o(m,0) = \left.\frac{\partial U_o}{\partial m}\right|_{m=\infty} = 0. \end{aligned}\right\} \tag{12}$$

This is readily solved by taking the Laplace transform of the system with respect to the variable τ . If

$$u(m,s) = \int_0^\infty e^{-s\tau} U_o(m,\tau)\, d\tau \equiv \mathcal{L}\,[U_o]$$

and

$$f(s) = \mathcal{L}\,[F],$$

the transformed system becomes

$$\left.\begin{aligned} &\frac{d^2u}{dm^2} - \frac{s}{D}\,u = 0, \\ &\left.\frac{d^2u}{dm^2}\right|_{m=0} = f(s), \qquad \left.\frac{du}{dm}\right|_{m=\infty} = 0, \end{aligned}\right\}$$

with solution

$$u = \frac{D}{s}\, f(s)\, e^{-m\sqrt{\frac{s}{D}}}.$$

Thus

$$\frac{du}{dm} = -\sqrt{\frac{D}{s}}\, f(s)\, e^{-m\sqrt{\frac{s}{D}}}, \qquad \frac{d^2u}{dm^2} = f(s)\, e^{-m\sqrt{\frac{s}{D}}},$$

giving

$$\theta_o = \mathcal{L}^{-1}\,[\tfrac{du}{dm}] = -\sqrt{\frac{D}{\pi}} \int_0^\tau \frac{F(\xi)\,d\xi}{\sqrt{\tau-\xi}}\, e^{-\frac{m^2}{4D(\tau-\xi)}}, \tag{13}$$

$$\frac{\partial^2 U_o}{\partial m^2} = \mathcal{L}^{-1}\,[\tfrac{d^2u}{dm^2}] = \frac{m}{\sqrt{4\pi D}} \int_0^\tau \frac{F(\xi)\,d\xi}{(\tau-\xi)^{3/2}}\, e^{-\frac{m^2}{4D(\tau-\xi)}}, \tag{14}$$

The system for the perturbation correction U_1 may be written

$$\left.\begin{aligned} &\frac{\partial^2 U_1}{\partial m^2} - \frac{1}{D}\frac{\partial U_1}{\partial \tau} = G(m,\tau), \\ &\left.\frac{\partial^2 U_1}{\partial m^2}\right|_{m=0} = U_1(m,0) = \left.\frac{\partial U_1}{\partial m}\right|_{m=\infty} = 0, \end{aligned}\right\} \tag{15}$$

where

$$G(m, \tau) = \left(\frac{r^4}{R^4} - 1 \right) \left[\frac{\partial^2 U_o}{\partial m^2} + \frac{\partial^2 U_1}{\partial m^2} \right] . \tag{16}$$

If

$$v(m,s) = \mathcal{L}[U_1], \qquad g(m,s) = \mathcal{L}[G],$$

the transformed equations become

$$\left. \begin{aligned} &\frac{d^2 v}{dm^2} - \frac{s}{D} v = g(m,s), \\ &\left. \frac{d^2 v}{dm^2} \right|_{m=0} = \left. \frac{dv}{dm} \right|_{m=\infty} = 0, \end{aligned} \right\}$$

with solution

$$v = -\frac{1}{2}\sqrt{\frac{D}{s}} \left\{ e^{-m\sqrt{\frac{s}{D}}} \int_o^m e^{x\sqrt{\frac{s}{D}}} g(x,s)\, dx + e^{m\sqrt{\frac{s}{D}}} \int_m^\infty e^{-x\sqrt{\frac{s}{D}}} g(x,s)\, dx \right.$$

$$\left. - e^{-m\sqrt{\frac{s}{D}}} \int_o^\infty e^{-x\sqrt{\frac{s}{D}}} g(x,s)\, dx \right\},$$

so that

$$\frac{dv}{dm} = \frac{1}{2} \left\{ e^{-m\sqrt{\frac{s}{D}}} \int_o^m e^{x\sqrt{\frac{s}{D}}} g\, dx - e^{m\sqrt{\frac{s}{D}}} \int_m^\infty e^{-x\sqrt{\frac{s}{D}}} g\, dx \right.$$

$$\left. - e^{-m\sqrt{\frac{s}{D}}} \int_o^\infty e^{-x\sqrt{\frac{s}{D}}} g\, dx \right\} .$$

At the bubble wall $m = 0$, this reduces to

$$\left. \frac{dv}{dm} \right|_{m=0} = - \int_o^\infty e^{-x\sqrt{\frac{s}{D}}} g(x,s)\, dx,$$

giving for the perturbation temperature at the bubble wall*

$$\theta_1(0, \tau) = - \int_o^\infty dx \cdot \frac{x}{\sqrt{4\pi D}} \int_o^\tau \frac{G(x, \zeta)\, d\zeta}{(\tau - \zeta)^{3/2}} e^{-\frac{x^2}{4D(\tau - \zeta)}},$$

---

* It is assumed in the following discussion that all limiting procedures, changes of order of integration, etc., are permissible.

or from (16),

$$\theta_1(0,\tau) = -\frac{1}{\sqrt{4\pi D}} \int_0^{\tau} \frac{d\zeta}{(\tau-\zeta)^{3/2}} \int_0^{\infty} x e^{-\frac{x^2}{4D(\tau-\zeta)}}$$

$$\times \left(\frac{r^4}{R^4} - 1\right) \left[\frac{\partial^2 U_o}{\partial x^2} + \frac{\partial^2 U_1}{\partial x^2}\right] dx. \tag{17}$$

The integral equation for the perturbation potential correction U_1 will be given for completeness. Its Laplace transform $v(m,s)$ can be written in the form

$$v = -\frac{1}{2}\sqrt{\frac{D}{s}} \int_0^{\infty} \left[e^{-|m-x|\sqrt{\frac{s}{D}}} - e^{-(m+x)\sqrt{\frac{s}{D}}}\right] g(x,s)\, dx,$$

from which one obtains

$$U_1 = -\frac{1}{2}\sqrt{\frac{D}{\pi}} \int_0^{\tau} \frac{d\zeta}{\sqrt{\tau-\zeta}} \int_0^{\infty} \left[e^{-\frac{(m-x)^2}{4D(\tau-\zeta)}} - e^{-\frac{(m+x)^2}{4D(\tau-\zeta)}}\right]$$

$$\times \left(\frac{r^4}{R^4} - 1\right) \left[\frac{\partial^2 U_o}{\partial x^2} + \frac{\partial^2 U_1}{\partial x^2}\right] dx.$$

The solutions given above in eqs. (13)-(17) are thus far exact, but not useful for computation. The approximations to be made depend upon the assumption that the influence of the heat exchange occurring at the bubble wall does not extend far into the liquid. The transform of the unperturbed temperature solution may also be written

$$\frac{du}{dm} = \left.\frac{du}{dm}\right|_{m=0} e^{-m\sqrt{\frac{s}{D}}},$$

which yields

$$\theta_o(m,\tau) = \frac{m}{\sqrt{4\pi D}} \int_0^{\tau} \frac{\theta_o(0,\zeta)\, d\zeta}{(\tau-\zeta)^{3/2}} \; e^{-\frac{m^2}{4D(\tau-\zeta)}}. \tag{18}$$

For either the expanding or collapsing bubble, $|\theta_o(0,\zeta)|$ is an increasing function of ζ. Hence, if $\theta_o(0,\zeta)$ may be considered negligible for $\zeta < \tau_o$ ($< \tau$), one obtains from eq. (18) the inequality

$$|\theta_o(m, \tau)| \le |\theta_o(0, \tau)| \operatorname{erfc}\left(\frac{m}{\sqrt{4D(\tau - \tau_o)}}\right) \qquad (\tau > \tau_o).$$

Since $\operatorname{erfc}(x) < 1/2$ for $x > .5$, the characteristic diffusion length in terms of the Lagrangian coordinates may be taken to be $m = \sqrt{D(\tau - \tau_o)}$ for the unperturbed temperature solution. The parameter of the perturbation is

$$\frac{r^4}{R^4} - 1 = \left(1 + \frac{3m}{R^3}\right)^{4/3} - 1,$$

which in the region of significant temperature variation is therefore less than

$$\left(1 + \frac{3\sqrt{D(\tau - \tau_o)}}{R^3}\right)^{4/3} - 1.$$

Thus the perturbation correction may be expected to be small in comparison with the unperturbed solution when $3\sqrt{D(\tau - \tau_o)}/R^3$ is small in comparison with unity, which will be the case if D is sufficiently small. The perturbation correction must vanish when θ_o vanishes (e.g. for $\tau < \tau_o$) because of the boundary and initial conditions on the perturbation equation.

For the growing bubble, $\tau - \tau_o \le R^4(t)(t - t_o)$, so that

$$\frac{3\sqrt{D(\tau - \tau_o)}}{R^3} \le \frac{3\sqrt{D(t - t_o)}}{R} .$$

The significant heat transfer for the 103^o bubble begins at about $t_o = .15$ millisec. The bubble radius is 2×10^{-3} cm about .06 millisec later. Taking $D = 1.9 \times 10^{-3}$ cm^2/sec, this gives

$$\frac{3\sqrt{D(t - t_o)}}{R} \approx .50$$

near the beginning of the 103^o bubble growth. The ratio drops asymptotically to .20 at later times. Thus within the boundary layer, the perturbation parameter $(r^4/R^4) - 1$ is certainly smaller than .50 during the time of significant heat exchange at the bubble wall. For larger initial superheats the bubble grows faster, and the ratio is accordingly somewhat smaller. For the collapsing bubble considered here, the ratio $\frac{3\sqrt{D(\tau - \tau_o)}}{R^3}$ is much smaller than unity except near the point of collapse.

When the thin thermal boundary layer assumption is valid, one may approximate the perturbation parameter by

$$\left(1 + \frac{3m}{R^3}\right)^{4/3} - 1 \approx \frac{4m}{R^3}$$

within the region of significant heat transfer, and to a first approximation neglect the $\partial^2 U_1/\partial x^2$ term (which vanishes in any case at the bubble wall) in comparison with the $\partial^2 U_o/\partial x^2$ term within the perturbation solution integrals. Thus, the perturbation temperature correction at the bubble wall eq. (17) becomes approximately

$$\theta_1(0, \tau) = -\frac{1}{\sqrt{4\pi D}} \int_0^{\tau} \frac{d\varsigma}{(\tau - \varsigma)^{3/2}} \int_0^{\infty} x e^{-\frac{x^2}{4D(\tau - \varsigma)}} \frac{4x}{R^3} \frac{\partial^2 U_o}{\partial x^2} dx,$$

or by eq. (14),

$$\theta_1(0, \tau) = -\frac{1}{\pi D} \int_0^{\tau} \frac{d\varsigma}{R^3(\varsigma)(\tau - \varsigma)^{3/2}} \int_0^{\infty} x^3 e^{-\frac{x^2}{4D(\tau - \varsigma)}} dx$$

$$\times \int_0^{\varsigma} \frac{F(\xi)\, d\xi}{(\varsigma - \xi)^{3/2}} e^{-\frac{x^2}{4D(\varsigma - \xi)}} .$$

Interchanging the order of the last two integrations gives

$$\theta_1(0, \tau) = -\frac{1}{\pi D} \int_0^{\tau} \frac{d\varsigma}{R^3(\tau - \varsigma)^{3/2}} \int_0^{\varsigma} \frac{F(\xi)\, d\xi}{(\varsigma - \xi)^{3/2}} \int_0^{\infty} x^3 e^{-\frac{x^2(\tau - \xi)}{4D(\tau - \varsigma)(\varsigma - \xi)}} dx$$

$$= -\frac{1}{\pi D} \int_0^{\tau} \frac{d\varsigma}{R^3(\tau - \varsigma)^{3/2}} \int_0^{\varsigma} \frac{F(\xi)\, d\xi}{(\varsigma - \xi)^{3/2}} \cdot \frac{8D^2(\tau - \varsigma)^2(\varsigma - \xi)^2}{(\tau - \xi)^2}$$

$$= -\frac{8D}{\pi} \int_0^{\tau} \frac{\sqrt{\tau - \varsigma}\, d\varsigma}{R^3(\varsigma)} \int_0^{\varsigma} \frac{\sqrt{\varsigma - \xi}\, F(\xi)\, d\xi}{(\tau - \xi)^2} . \tag{19}$$

According to eqs. (2), (11),

$$F(\tau) = \frac{L}{3k} \frac{d}{d\tau} [R^3 \rho_{eq}] \tag{20}$$

is proportional to the rate of increase of the mass of vapor within the bubble, in terms of the time variable

$$\tau = \int_0^t R^4(t)\, dt.$$

$F(\tau)$ is therefore negligible until a time $t = t_o$ or $\tau = \tau_o$ when the radius of the bubble begins to change, so that the lower limits of integration in eq. (19) may be taken to be $\xi = \zeta = \tau_o$ instead of 0.

For the collapsing bubble, $|F(\tau)|$ is itself an increasing function of τ. For the expanding bubble, $R \sim C\sqrt{t}$ as $t \to \infty$ (see Eq. IV(62)), so that after an initial increase $F(\tau)$ eventually tends to zero as $\tau^{-1/2}$; however, for a reasonable choice of τ_o, the product $\sqrt{\tau - \tau_o}\, F(\tau)$ in this case becomes an increasing function of τ. Hence, the perturbation temperature correction given by eq. (19) is bounded by

$$-\theta_1(0, \tau) = \frac{8D}{\pi} \int_{\tau_o}^{\tau} \frac{\sqrt{\tau - \zeta}\, d\zeta}{R^3(\zeta)} \int_{\tau_o}^{\zeta} \sqrt{\xi - \tau_o}\, F(\xi) \cdot \frac{\sqrt{\zeta - \xi}\, d\xi}{(\tau - \xi)^2 \sqrt{\xi - \tau_o}}$$

$$\leq \frac{8D}{\pi} \int_{\tau_o}^{\tau} \frac{F(\zeta)\, d\zeta}{R^3(\zeta)} \cdot \sqrt{\tau - \zeta}\ \sqrt{\zeta - \tau_o} \int_{\tau_o}^{\zeta} \frac{\sqrt{\zeta - \xi}\, d\xi}{(\tau - \xi)^2 \sqrt{\xi - \tau_o}} \tag{21}$$

for the expanding bubble, or its negative for the collapsing bubble. The last integtal in (21) can be transformed by the change of variables

$$\xi = \tau_o + \frac{(\tau - \tau_o)(\zeta - \tau_o)(1 - x)}{(\tau - \tau_o) - (\zeta - \tau_o)x} \qquad (0 < x < 1)$$

to

$$\sqrt{\tau - \zeta}\ \sqrt{\zeta - \tau_o} \int_{\tau_o}^{\tau} \frac{\sqrt{\zeta - \xi}\ d\xi}{(\tau - \xi)^2\ \sqrt{\xi - \tau_o}}$$

$$= \left(\frac{\zeta - \tau_o}{\tau - \tau_o}\right)^{3/2} \int_0^1 \frac{\sqrt{x}\, dx}{\sqrt{1 - x}} = \frac{\pi}{2} \left(\frac{\zeta - \tau_o}{\tau - \tau_o}\right)^{3/2},$$

giving for (21)

$$| \theta_1(0,\tau)| \leq 4D \int_{\tau_0}^{\tau} \left(\frac{\xi-\tau_0}{\tau-\tau_0}\right)^{3/2} \frac{|F(\xi)|d\xi}{R^3(\xi)}. \tag{22}$$

By (20), this may be written as

$$|\theta_1(0,\tau)| \leq \int_{\tau_0}^{\tau} \left(\frac{\xi-\tau_0}{\tau-\tau_0}\right)^{3/2} \frac{4DL}{3kR^3(\xi)} \frac{|d[R^3(\xi)\rho_{eq}]|}{d\xi} d\xi$$

$$= \int_{\tau_0}^{\tau} \frac{\sqrt{\xi-\tau_0}\, d\xi}{(\tau-\tau_0)^{3/2}} \cdot \frac{4DL\rho_{eq}}{3k} \left|\frac{d\ \ln[R^3(\xi)\rho_{eq}]}{d\ \ln(\xi-\tau_0)}\right|;$$

or if we neglect the variation of $\rho_{eq}(T)$ in comparison with that of R^3 in the estimate, as

$$|\theta_1(0,\tau)| \leq \frac{4DL\rho_{eq}}{3k} \int_{\tau_0}^{\tau} \frac{\sqrt{\xi-\tau_0}\, d\xi}{(\tau-\tau_0)^{3/2}} \left|\frac{d\ \ln R^3(\xi)}{d\ \ln(\xi-\tau_0)}\right|. \tag{23}$$

For water, the factor

$$\frac{4DL\rho_{eq}}{3k}$$

in (23) has the value $.066^\circ$C at $T = 50^\circ$C, and $.50^\circ$C at $T = 100^\circ$C.

In the case of the collapsing bubble, the ratio of logarithmic derivatives in (23) is small except near the point of collapse, when it increases rapidly in absolute value. Since

$$\frac{\sqrt{\xi-\tau_0}}{(\tau-\tau_0)^{3/2}} < \frac{1}{\xi-\tau_0}$$

for $\tau_0 < \xi < \tau$, a crude bound for $|\theta_1|$ for the collapsing bubble is

$$|\theta_1| < \frac{4DL\rho_{eq}}{3k} \int_{\tau_0}^{\tau} d\ \ln(\xi-\tau_0) \left|\frac{d\ \ln R^3(\xi)}{d\ \ln(\xi-\tau_0)}\right|$$

$$= \frac{4DL\rho_{eq}}{3k} \ln\left(\frac{R_0^3}{R^3}\right). \tag{24}$$

This has about the value $.07^\circ C \times 6.9 \approx .5^\circ C$ for the bubble considered here when the bubble radius has dropped to 1/10 of its initial value, which is farther than the collapse was actually followed (see Fig. 11). However, the actual temperature rise (see Fig. 12) at the end of the time period considered was $40^\circ C$, in comparison with which the perturbation correction estimate is completely negligible.

For the expanding bubble, the ratio of logarithmic derivatives appearing in eq. (23) vanishes at $\zeta = \tau_0$, rises to a maximum of less than .75 at some value of $\zeta > \tau_0$, then drops asymptotically to the value 1/2. The decrease after the maximum is sufficiently gradual that it can be dominated by a factor $(\zeta - \tau_0)^\varepsilon$ for a small value of ε. Thus, a bound on $|\theta_1|$ for the expanding bubble is given by

$$
\begin{aligned}
|\theta_1| &\leq \frac{4DL\rho_{eq}}{3k} \int_{\tau_0}^{\tau} \frac{(\zeta - \tau_0)^{1/2-\varepsilon}\, d\zeta}{(\tau - \tau_0)^{3/2}} (\zeta - \tau_0)^\varepsilon \frac{d \ln R^3}{d \ln(\zeta - \tau_0)} \\
&\leq \frac{4DL\rho_{eq}}{3k} (\tau - \tau_0)^\varepsilon \frac{d \ln R^3(\tau)}{d \ln(\tau - \tau_0)} \int_{\tau_0}^{\tau} \frac{(\zeta - \tau_0)^{1/2-\varepsilon}\, d\zeta}{(\tau - \tau_0)^{3/2}} \\
&= \frac{4DL\rho_{eq}}{3k} \frac{1}{3/2 - \varepsilon} \frac{d \ln R^3(\tau)}{d \ln(\tau - \tau_0)}.
\end{aligned}
\tag{25}
$$

Taking τ_0 for the 103° bubble to correspond to $t_0 = .15$ millisec (see Fig. 7), we find for the ratio of logarithmic derivatives in (25) a maximum of .71 at $t \approx .19$ millisec., and the value $\varepsilon \approx .15$. The bound on $|\theta_1|$ thus has a maximum of about $.26^\circ C$ at .19 millisec, and drops asymptotically to $.18^\circ C$. For the 106° bubble (Fig. 9) the choice $t_0 = 28$ microsec. gives a maximum ratio of .74 at 34 microsec. and the value $\varepsilon = .25$. Since $4DL\rho_{eq}/3k \approx .60^\circ C$ at $106^\circ C$, the bound on $|\theta_1|$ for the 106° bubble has a maximum value $.36^\circ C$ and an asymptotic value $.24^\circ C$.

The conclusions drawn from the analysis above of the perturbation parameter, and from the bounds derived for the perturbation temperature correction at the bubble wall, are thus in agreement. They indicate that the thin thermal boundary layer assumption is valid when the vapor bubble grows or collapses rapidly, and also may be considered valid when the bubble is nearly in equilibrium. The assumption becomes somewhat critical, in the case of water above its boiling point, when the bubble growth occurs at an intermediate rate - sufficiently rapid that significant heat transfer occurs at the bubble wall, but slow enough for the liquid to partially adjust to this transfer. The error incurred at this critical stage, however, does not amount to more than a few tenths of a degree, and remains a small fraction of the actual temperature. It is sufficient, therefore, to use the unperturbed temperature solution in the dynamic problem, at least for the case of water.

In terms of the original time and radius variables, the unperturbed temperature solution (13) is

$$\theta_o(r,t) = T(r,t) - T_\infty = -\sqrt{\frac{D}{\pi}} \int_0^t \frac{R^2(x)\left.\frac{\partial T}{\partial r}\right|_{r=R(x)} dx}{\sqrt{\int_x^t R^4(y)\,dy}}$$

$$\times \exp\left[- \frac{(r^3 - R^3(x))^2}{36D \int_x^t R^4(y)\,dy} \right],$$

which reduces at the bubble wall to

$$\theta_o(R,t) = -\sqrt{\frac{D}{\pi}} \int_0^t \frac{R^2(x)\left.\frac{\partial T}{\partial r}\right|_{r=R(x)} dx}{\sqrt{\int_x^t R^4(y)\,dy}} .$$

The temperature gradient at the bubble wall is given in terms of the evaporation rate by eqs. (1), (2), so that for the present problem, the unperturbed solution becomes

$$\theta_o(R,t) = -\frac{L}{3k}\sqrt{\frac{D}{\pi}} \int_0^t \frac{\frac{d}{dx}(R^3\rho_{eq})\,dx}{\sqrt{\int_x^t R^4(y)\,dy}} . \qquad (26)$$

Diffusion Solutions.

It is of interest to compare with the convection solution presented above, a diffusion approximation (for the identical physical problem) proposed by Forster and Zuber.[7,14] This approximation may be developed in the following manner.*

The heat equation (5) for an incompressible fluid may be written

$$\rho c_v \frac{\partial \theta}{\partial t} = \nabla \cdot [k\nabla\theta - \underline{v}\rho c_v \theta]. \tag{27}$$

In this form, one may identify the last term on the right as representing the rate of heat influx into an elementary volume fixed in space due to transport by the fluid. If the fluid velocity is sufficiently small, the transport effect may be neglected in comparison with conduction effects, represented by the first term on the right. With this neglect, the equation becomes a diffusion equation,

$$\nabla^2\theta = \frac{1}{D}\frac{\partial \theta}{\partial t}, \qquad (D = \frac{k}{\rho c_v}). \tag{28}$$

The initial and external boundary conditions for eq. (28)

$$\theta(r,0) = \theta(\infty, t) = 0 \tag{29}$$

are the same as for the convection equation. The boundary condition at the moving vapor bubble wall

$$- k \cdot 4\pi R^2 \left.\frac{\partial \theta}{\partial r}\right|_{r=R(t)} = -L \frac{d}{dt}\left(\frac{4}{3}\pi R^3 \rho_{eq}\right) \tag{30}$$

is also the same, but becomes extremely difficult to apply in Eulerian coordinates, and some sort of physical or mathematical artifice must be resorted to if a solution in closed form is to be obtained. The approach to the problem given by Forster and Zuber consists of treating the heat exchange at the bubble wall as though it were due to a moving spherical heat source (for the collapsing bubble, or a heat sink for the expanding bubble) in a stationary infinite fluid.

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* The presentation given here is not that of the authors. The original presentation of Forster and Zuber (ref. (7)) is quite brief; the second (ref. (14)) by Forster purports to give a more detailed treatment of the problem, but actually treats a different problem. Neither paper gives an adequate analysis.

They start with the elementary solution*

$$\theta = \frac{Q}{4\pi r r' \sqrt{\pi D t}} \left[e^{-\frac{(r-r')^2}{4Dt}} - e^{-\frac{(r+r')^2}{4Dt}} \right] \tag{31}$$

of equations (28), (29) for the temperature difference θ in the fluid at any radius r and any time $t > 0$ due to an instantaneous spherical heat source at $r = r'$, $t = 0$. The total heat liberated is $2\rho c_v Q$. This is to be related to the quantity of heat transferred out of the bubble by condensation during a time interval dx while the bubble radius is $r' = R(x)$. The actual heat h transferred out of the bubble at time $t = x$ is given by the right side of eq. (30).

$$h = -L \frac{d}{dx} [\tfrac{4}{3} \pi R^3(x) \rho_{eq}] \, dx, \tag{32}$$

and this is also the heat transferred into the liquid at $t = x$. In accordance with the Forster and Zuber assumption of an infinite medium, however, the elementary heat source associated with the solution (31) releases its heat not only to the fluid outside the shell $r = r'$, but also to that part of the fluid inside the shell. At the instant of release, half of the heat appears inside the shell. Therefore, if the solution (31) is to correspond to the heat release outside the shell at the moment of liberation, the h of eq. (32) must be equated to only half of the total heat liberated, giving

$$Q = \frac{h}{\rho c_v} = -\frac{4\pi L}{3\rho c_v} \frac{d}{dx} [R^3 \rho_{eq}] \, dx. \tag{33}$$

This choice introduces an error at later times in the final solution for two reasons: First of all, the heat flowing through a later shell is no longer just that due to condensation at that time, but still has a contribution from the heat diffusing outward from the shell $r = r'$. This relaxation effect is minimal if the radial velocity of the bubble wall is large, and/or the thermal conductivity of the (stationary) fluid

---

* Eq. (31) is readily obtained by the operational methods already used. It differs from the standard solution given by Carslaw and Jaeger, Conduction of Heat in Solids (Oxford Univ. Press, 1947), p. 219, by a factor of two because of the choice $2\rho c_v Q$, rather than $\rho c_v Q$, for the total heat liberated. The transform of (31) is given below.

is small. Unfortunately, these are not the conditions of validity of the diffusion model. Secondly, there is still the contribution to the heat content of the liquid at later times by the heat liberated within the shell $r = r'$. The heat released within the shell ultimately reverses its direction of flow and adds to the heat content outside the shell. This effect can be eliminated by a simple device to be described below. Elimination of the relaxation effect is a more involved matter.

The Forster and Zuber solution is obtained by replacing t by $t - x$ in eq. (31) (corresponding to a heat release at $t = x$, rather than $t = 0$) and r' by $R(x)$, using (33) to define Q, and integrating the result over all sources from $x = 0$ to $x=t$, This gives for the temperature difference at the bubble wall $r = R(t)$,

$$\theta(R,t) = -\frac{L}{3\rho c_v \sqrt{\pi D}} \int_0^t \frac{\frac{d}{dx}(R^3\rho_{eq})\,dx}{R(t)\,R(x)\,\sqrt{t-x}}$$

$$\times \left\{ e^{-\frac{[R(t)-R(x)]^2}{4D(t-x)}} - e^{-\frac{[R(t)+R(x)]^2}{4D(t-x)}} \right\} . \qquad (34)$$

Assuming that, for the dynamic problem under consideration (the growing bubble), the second exponential in (34) can be neglected and the first replaced by unity, Forster and Zuber further reduce the above equation to the form*

$$\theta(R,t) = -\frac{L}{3\rho c_v \sqrt{\pi D}} \int_0^t \frac{\frac{d}{dx}(R^3\rho_{eq})\,dx}{R(t)\,R(x)\sqrt{t-x}} . \qquad (35)$$

A somewhat different approach to the diffusion problem with the moving boundary, for which the difficulty connected with the heat release inside the boundary does not arise, is the following: Let it be supposed that at $t = 0$, a (mathematical) shutter opens at $r = r'$, such as to pass through the shell a prescribed quantity of heat h, then instantaneously closes again. The effect of the moving boundary can then be obtained, as above, by integrating over successive shutters at $r' = R(x)$, $0 < x < t$.

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* Both papers by Forster attempt to justify the formula (35) as an approximation to the solution of the diffusion problem, and then as an approximate solution to the convection problem. The convection approximation (26) was already available, and, in fact, referred to in both papers.

The "shutter condition" can be obtained by noting that the heat flow through a surface element bounding the fluid is determined (as for the convection solution) by the temperature gradient there. The appropriate boundary condition for a shutter at $r = r'$, $t = 0$ will thus be of the form

$$-\left.\frac{\partial\theta}{\partial r}\right|_{r=r'} = Q'\delta(t). \tag{36}$$

The constant Q' can be related to the heat h passed by the shutter by a determination of the total heat outside the shell at a later time $(t > 0)$.

The system of equationsto be solved is

$$\left.\begin{aligned} &\nabla^2\theta = \frac{1}{D}\frac{\partial\theta}{\partial t} \qquad (r > r'), \\ &\theta(r,0) = \theta(\infty\,,\, t) = 0, \qquad \left.\frac{\partial\theta}{\partial r}\right|_{r=r'} = -Q'\delta(t). \end{aligned}\right\} \tag{37}$$

By putting $w = \mathcal{L}\,[\theta]$ and taking the Laplace transform of the system with respect to t, one can reduce it to an equivalent system

$$\left.\begin{aligned} &\frac{d^2}{dr^2}(rw) = \frac{s}{D}(rw), \\ &w(\infty\,,\, s) = 0, \qquad \left.\frac{dw}{dr}\right|_{r=r'} = -\,Q', \end{aligned}\right\}$$

with solution

$$w(r,s) = \frac{r'^2\,Q'}{1 + r'\sqrt{\frac{s}{D}}} \cdot \frac{1}{r}\, e^{-(r-r')\sqrt{\frac{s}{D}}} \qquad (r > r'). \tag{38}$$

The heat liberated outside the shell $r = r'$ is given by

$$\mathcal{L}\,[h] = \int_{r'}^{\infty} \rho\, c_v w \cdot 4\pi r^2\, dr = 4\pi r'^2 \rho\, c_v Q' \cdot \frac{D}{s}\;,$$

i.e.

$$h = 4\pi r'^2 \rho\, c_v Q' D,$$

so that (38) becomes

$$w(r,s) = \frac{h}{4\pi\rho c_v D} \cdot \frac{1}{r}\; \frac{e^{-(r-r')\sqrt{\frac{s}{D}}}}{1 + r'\sqrt{\frac{s}{D}}}\,, \tag{39}$$

which has the inverse transform

$$Q = \frac{h}{4\pi\rho c_v r r' \sqrt{\pi D t}} \left\{ e^{-\frac{(r-r')^2}{4Dt}} - \frac{\sqrt{\pi D t}}{r'}\, e^{\frac{Dt}{r'^2} - (\frac{r}{r'} - 1)}\, \operatorname{erfc}\left[\frac{\sqrt{Dt}}{r'} + \frac{r - r'}{\sqrt{4Dt}}\right] \right\}. \tag{40}$$

The analogue of the moving source solution (34) can be obtained from (40) by again writing $t - x$ for t, $R(x)$ for r', $R(t)$ for r, using eq. (32) for h, and integrating over x. The moving shutter analogue is thus

$$\theta = -\frac{L}{3\rho c_v \sqrt{\pi D}} \int_0^t \frac{\frac{d}{dx}(R^3 \rho_{eq})\, dx}{R(x)\, R(t)\, \sqrt{t-x}} \left\{ e^{-\frac{[R(t)-R(x)]^2}{4D(t-x)}} - \frac{\sqrt{\ (t-x)}}{R(x)}\, e^{\frac{D(t-x)}{R^2(x)} + \frac{R(t)}{R(x)} - 1}\, \operatorname{erfc}\left[\frac{\sqrt{D(t-x)}}{R(x)} + \frac{R(t)-R(x)}{\sqrt{4D(t-x)}}\right] \right\}. \tag{41}$$

This solution has, of course, the same difficulty with the relaxation heat flow that the moving source solution has, but the problem associated with the heat flow from within the moving boundary has been eliminated.

It is possible, in principle, to eliminate the relaxation heat flow from the shutter solution by using the correct boundary condition at the bubble wall. This can be done, for instance, by leaving h undetermined in (40), but summing the gradients of the elementary shutter solutions over the variable x to obtain the temperature gradient of the final solution in terms of the unknown differential $h(x)$. By using eq. (30) to specify the temperature gradient at the bubble wall, one obtains an integral equation to be solved for $h(x)$. The same procedure can be carried out for the moving source solution, leading again to an integral equation for $h(x)$. It is apparent, however, that a more appropriate procedure would be to return to the original equations and to attempt to solve them, using the correct boundary conditions from the beginning.

The moving source solution (34) and the shutter analogue (41) differ from one another in the last terms of the respective integrands. Since this difference accounts for the false heat flow from within the interior of the bubble in the case of the moving source solution, it may be expected to become important whenever relaxation effects become important, i.e., when the thermal diffusivity of the fluid is large. This may be verified indirectly by showing that the solutions become identical when the diffusivity is small. (A direct verification will be given below for the case of the growing vapor bubble.) Perhaps the easiest way to show this is to examine the Laplace transforms of the respective elementary solutions. If the transform of (40) is denoted by w, as above, and that of (31) by u, one has

$$w(r,s) = \frac{h}{4\pi\rho c_v D} \cdot \frac{1}{r} \left[\frac{e^{-(r-r')\sqrt{\frac{s}{D}}}}{1 + r'\sqrt{\frac{s}{D}}} \right] \qquad (r > r'),$$

$$u(r,s) = \frac{h}{4\pi\rho c_v D} \cdot \frac{1}{r} \quad \frac{e^{-|r-r'|\sqrt{\frac{s}{D}}} - e^{-(r+r')\sqrt{\frac{s}{D}}}}{r'\sqrt{\frac{s}{D}}} \qquad (r > 0).$$

In the equation for u, the substitution $Q = h/\rho c_v$ has been made. It will be observed that for $r > r'$, $r'\sqrt{\frac{s}{D}} >> 1$, both reduce to the form

$$\frac{h}{4\pi\rho c_v D} \; \frac{e^{-(r-r')\sqrt{\frac{s}{D}}}}{rr'\sqrt{\frac{s}{D}}},$$

which has the inverse transform

$$\theta = \frac{h}{4\pi \rho c_v \, rr' \, \sqrt{\pi Dt}} \; e^{-\frac{(r-r')^2}{4Dt}} .$$

The contribution to the boundary temperature by this elementary solution is

$$\theta = - \frac{L}{3\rho c_v \sqrt{\pi D}} \int_0^t \frac{\frac{d}{dx}(R^3 \rho_{eq}) \, dx}{R(x) \, R(t) \, \sqrt{t-x}} \; e^{-\frac{[R(t)-R(x)]^2}{4D(t-x)}} , \tag{42}$$

i.e. the leading term of the solutions (34), (41).

The solution (42) is a valid approximation to (34) and (41), however, only for small D. For large D, the remaining terms in (34), (41) become important; as D tends to finity, the integrands of both (34) and (41) tend to zero, in fact, for $x \neq t$. Eq. (42), on the other hand, tends to the Forster and Zuber approximation (35) with large D. It is to be concluded from this that the Forster and Zuber approximation is never a valid approximation to either of the diffusion solutions (except in the case of a quasi-stationary bubble $R(t) \approx$ constant). When it is permissible to neglect the second exponential in eq. (34) in comparison with the first, the first exponential cannot be set equal to unity; and when the first exponential approaches unity, so does the second.

General Comparison of the Convection and Diffusion Solutions.

The temperature solutions presented above have not been restricted thus far by a radius-time relation, and so may be compared for any assumed behavior of the boundary consistent with the heat problem (such as may be achieved, for instance, by keeping the temperature of the bulk liquid at T_o but varying the external pressure).

For a growing bubble, the convection solution (26) predicts a temperature drop at the bubble wall which varies inversely as the square root of the thermal diffusivity D of the liquid, other factors (such as the specific $R(t)$ behavior) being held constant. The diffusion solutions (34), (41) predict a smaller drop than the convection solution for all D. The discrepancy becomes most marked for small D, when the convection drop becomes large but the diffusion drops tend (depending upon the law of growth) to vanish.

These predictions are qualitatively understandable on the basis of the physical models involved. In the case of the convection model, the heat source (or sink) is always located at the same fluid elements, those at the bubble wall. Thus, a decrease in the diffusivity has the effect of concentrating the region within which significant heat transfer occurs nearer to the boundary, and correspondingly the temperature drop will be greater there (if the bubble is growing, or the temperature rise greater there when the bubble is collapsing) for small D than for large D. In the case of the diffusion model, on the other hand, the fluid remains stationary while the heat source sweeps through it. A decrease in the diffusivity here may ultimately be expected to have the effect of insulating the successive elementary sources from one another, such as to prevent any accumulation of heat from taking place.

When the diffusivity of the fluid is large, the relative importance of convection effects in comparison with diffusion effects should diminish. As has been pointed out above, the discrepancy between the convection and diffusion solutions is most marked at low, rather than high values of the diffusivity. However, both the convection and diffusion solutions presented here cease to be valid when the diffusivity is too large, so that a comparison in the limit of large D is not meaningful.

Comparison for Free Bubble Growth.

When the bubble growth is not forced by external pressure variations, it becomes limited eventually by the heat transfer at the bubble wall. The physical relations holding in the heat-limited growth will be discussed later,* but may be briefly related here. The evaporation at the bubble wall necessary for bubble growth forces the temperature of the liquid there down toward the boiling point of the liquid at the external pressure. If the boiling point is denoted by T_b, and the temperature of the bulk liquid by T_o, the late growth of the bubble must then be such as to satisfy the asymptotic relation

$$\theta \sim -(T_o - T_b). \tag{43}$$

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* See the discussion of the asymptotic phase of bubble growth in section IV.

For every temperature solution presented here, the relation (43) restricts the late bubble growth to a law of the form

$$R(t) \sim C\sqrt{t} \qquad \text{as} \quad t \to \infty . \tag{44}$$

The rate of bubble growth is then essentially specified by the value of C.

Let the parameters S, λ be denoted by

$$S = \frac{\rho c_v \sqrt{\pi}\,(T_o - T_b)}{L\rho_{eq}(T_b)} , \qquad \lambda = \frac{C}{\sqrt{4D}} . \tag{45}$$

Then S is related to λ by an equation of the form

$$S = I(\lambda), \tag{46}$$

where $I(\lambda)$ denotes the temperature integral involved. For the convection solution (26), $I(\lambda)$ is given by

$$I(\lambda) = \lambda\sqrt{3} \int_0^1 \frac{\sqrt{x}\,dx}{\sqrt{1-x^3}} = \frac{\pi}{\sqrt{3}}\lambda ; \tag{47a}$$

for the moving source solution (34) by*

$$I(\lambda) = \lambda \int_0^1 \frac{dx}{\sqrt{1-x}} \left\{ e^{-\lambda^2\left[\frac{1-\sqrt{x}}{1+\sqrt{x}}\right]} - e^{-\lambda^2\left[\frac{1+\sqrt{x}}{1-\sqrt{x}}\right]} \right\}$$

$$= 4\lambda^2\sqrt{\pi}\left\{1 - \lambda\sqrt{\pi}\, e^{\lambda^2} \operatorname{erfc}(\lambda)\right\} , \tag{47b}$$

$$\sim \begin{cases} 4\lambda^2\sqrt{\pi}\,(1 - \lambda\sqrt{\pi} + \cdots) & \text{as} \quad \lambda \to 0 \quad (D \to \infty), \\ 2\sqrt{\pi}\,(1 - \frac{3}{2\lambda^2} + \cdots) & \text{as} \quad \lambda \to \infty \quad (D \to 0); \end{cases}$$

for the moving shutter solution (41) by

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* The integrals (47b), (47c) are evaluated in Appendix B.

$$I(\lambda) = \lambda \int_0^1 \frac{dx}{\sqrt{1-x}} \left\{ e^{-\lambda^2\left[\frac{1-\sqrt{x}}{1+\sqrt{x}}\right]} \right.$$

$$\left. - \frac{\sqrt{\pi}}{2\lambda} \sqrt{\frac{1-x}{x}} \; e^{\frac{1-x}{4\lambda^2 x} + \frac{1}{\sqrt{x}} - 1} \operatorname{erfc}\left[\frac{1}{2\lambda} \sqrt{\frac{1-x}{x}} + \lambda \sqrt{\frac{1-\sqrt{x}}{1+\sqrt{x}}} \right] \right\},$$

$$\sim \begin{cases} 2\lambda^2 \sqrt{\pi}\left(1 - \dfrac{\lambda}{\sqrt{\pi}} + \cdots\right) & \text{as} \quad \lambda \to 0 \quad (D \to \infty), \\ 2\sqrt{\pi}\left(1 - \dfrac{2}{\lambda^2} + \cdots\right) & \text{as} \quad \lambda \to \infty \quad (D \to 0); \end{cases} \qquad (47c)$$

and for the Forster and Zuber approximation (35) by

$$I(\lambda) = \lambda \int_0^1 \frac{dx}{\sqrt{1-x}} = 2\lambda. \qquad (47d)$$

It will be observed from (47b), (47c) that the moving source solution and shutter solution become asymptotically equal in the region of large λ (i.e. of small D, for a given value of C), but differ by a factor of two when λ is small (D large). This factor of two is to be attributed to the contribution to the heat content of the liquid by the false heat flow from within the bubble surface, which occurs in the case of the moving source solution (47b). This just doubles the expected content (and temperature difference) for large D.* It may also be noted that the Forster and Zuber approximation (47d) behaves differently in all ranges of λ from the moving source solution (47b) which it is supposed to approximate.

Physically, bubble growth with a given value of C but various values of D can be obtained by choosing liquids with differing thermal diffusivity, and adjusting the superheat in each to give the specified rate of growth. If one concentrates on a given liquid (with fixed D), the parameter which varies with the superheat becomes C, so that the analysis of the various temperature solutions for a given liquid is to be made on

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* The actual heat content here is negative, corresponding to the heat loss from the liquid at the surface of the growing bubble due to evaporation.

the basis of the dynamic situation which occurs in the respective physical models, and its dependence on the superheat.

When the law of growth (44), applies, the temperature at the bubble wall has dropped practically to the boiling temperature of the liquid at the external pressure. The bubble growth is maintained by a differential temperature (and therefore pressure) effect which vanishes with the radial velocity of the bubble wall, and which is negligible in comparison with the temperature difference $T_o - T_b$.* The physical constants ρ, c_v, L, ρ_{eq} and D characteristic of the liquid may here be given their values at the boiling point T_b. The asymptotic rate of bubble growth (the constant C in eq. (44)) for a given model is then determined by the relations (45), (46) and the superheat $T_o - T_b$ of the bulk liquid.

The thermal relaxation effects which make the boundary condition at the bubble wall inaccurate, in the case of the diffusion solutions, become important if the bubble wall moves too slowly. Since $I(\lambda)$ is in all cases an increasing function of λ, this means (according to eq. (46)) that the diffusion solutions do not represent the diffusion model at low superheats. At larger superheats, these solutions become adequate representations of the diffusion model. But since the radial velocity of the bubble wall increases with the superheat, the diffusion model itself becomes non-physical at larger superheats.

The adequacy of the convection solution may be determined from eq. (25). When the asymptotic law of bubble growth (44) applies, the ratio of logarithmic derivatives appearing in (25) is equal to 1/2. The perturbation correction to the convection solution (26) is therefore not larger than about $.2^oC$ for water, and accordingly is negligible for all but the lowest superheats, once the vapor bubble growth has reached the asymptotic stage. One may therefore consider the convection solution to be accurate in this phase of bubble growth.

A plot of the values of C predicted by the convection solution (47a) and the moving shutter solution (47c) for varying degrees of superheat T_o will be found in Fig. 2, for the case of water at one atmosphere external

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* If the differential temperature effect were ignored, the bubble growth required by the theory would appear paradoxical.

pressure. The parameters ρ, c_v, L, ρ_{eq} and D have all been given their values at $T_b = 100^\circ C$. The temperature integral (47c) for the moving shutter solution was integrated numerically. The breakdown of the diffusion model for water is clearly shown in Fig. 2. The diffusion model predicts an explosive bubble growth at only $.7^\circ C$ superheat, and affords no asymptotic solution at all above this.

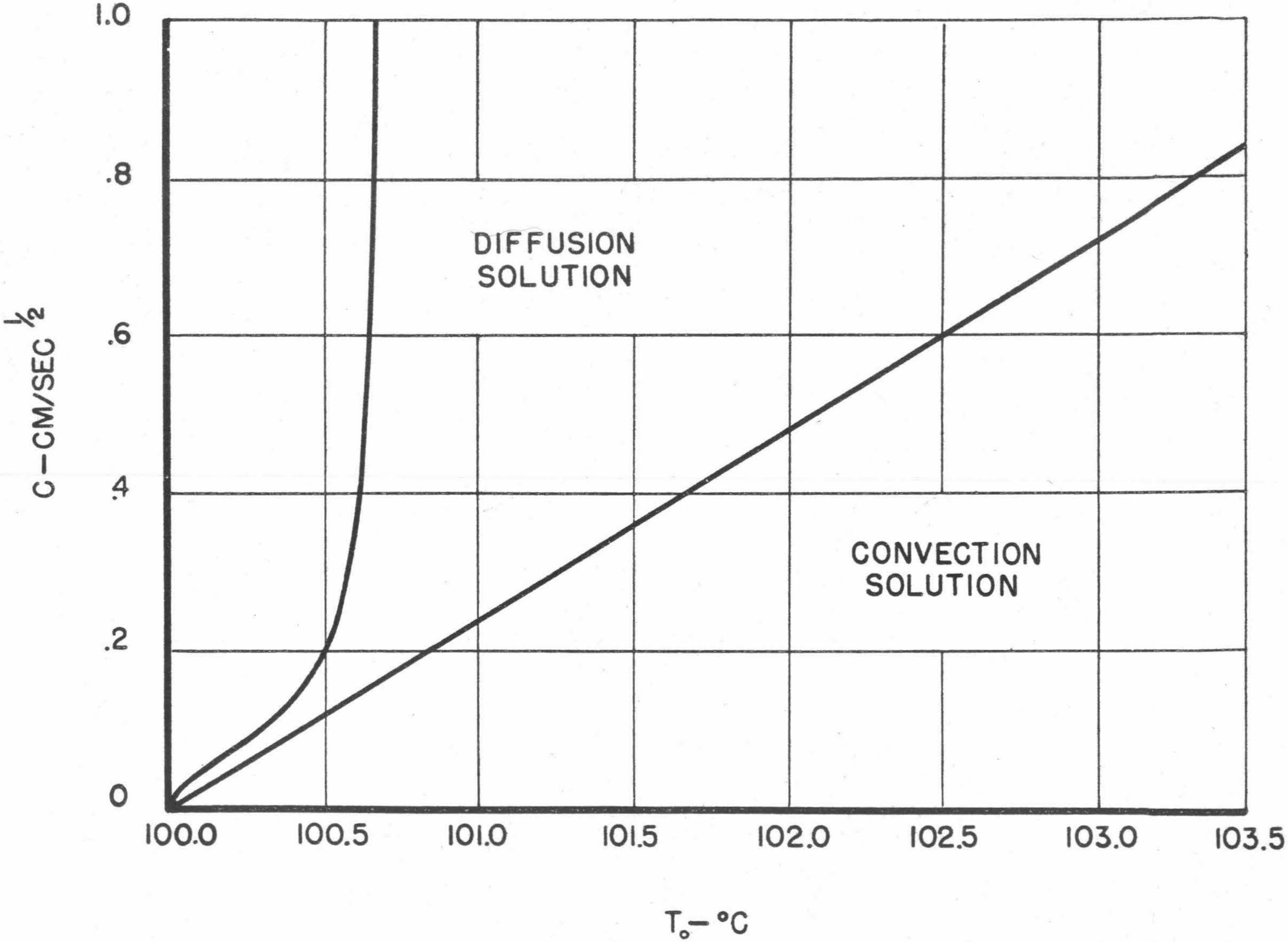

Fig. 2 - Asymptotic rate of bubble growth C (corresponding to the growth law $R \sim C\sqrt{t}$) predicted by the moving shutter diffusion solution and the convection solution for water at 1 atm. external pressure, as a function of the water superheat temperature T_o.

IV. THE DYNAMIC PROBLEM

The equation of motion of the vapor bubble wall is given by eq. II(68),

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{p_{eq}(T) - p_\infty}{\rho_{liq}} - \frac{2\sigma}{\rho_{liq}R}, \tag{1}$$

where R denotes the radius of the bubble wall at time t, $\dot{R}$ the radial velocity and $\ddot{R}$ the radial acceleration. The initial conditions for the bubbles considered here will be that the bubble starts from rest with radius R_o,

$$R(0) = R_o, \qquad \dot{R}(0) = 0. \tag{2}$$

In the case of the growing vapor bubble, it will further be assumed that the bubble is initially in (unstable) equilibrium, in which case the radius R_o becomes determined by the equation of motion. For the collapsing bubble, equilibrium conditions will not be assumed, so that the initial radius remains in this case arbitrary.

The surface tension parameter σ and the density ρ of the liquid will be assumed constant, and equal to their values at the initial liquid temperature T_o. The external pressure will also be assumed constant. The equilibrium vapor pressure of the liquid $p_{eq}(T)$ at the temperature T of the bubble wall cannot be assumed constant, however, since it is the pressure difference $p_{eq} - p_\infty$ appearing in eq. (1) which supplies the driving force for the expanding bubble, and this has been assumed to be in initial equilibrium with the surface tension. For the case of the collapsing bubble, the temperature at the bubble wall rises sharply near the point of collapse, and the corresponding rise of vapor pressure within the bubble may be expected to influence the rate of collapse.

The dependence of the equilibrium vapor pressure on temperature can be taken from equilibrium vapor pressure tables, so that $p_{eq}(T)$ may be assumed to be a known function of the temperature at the bubble wall. The equation of motion then becomes determinate when the bubble wall temperature is specified in terms of the parameters of bubble growth or collapse. This specification will here be assumed to be given by the unperturbed convection solution, eq. III(26):

$$T(R,t) = T_\infty - \frac{L}{3k}\sqrt{\frac{D}{\pi}} \int_0^t \frac{\frac{d}{dx}(R^3\rho_{eq})\,dx}{\sqrt{\int_x^t R^4(y)\,dy}}, \tag{3}$$

where, by eq. III(3), the temperature at $r = \infty$ is

$$T_\infty = T_o + \frac{D}{k}q(t), \qquad (q(0) = 0). \tag{4}$$

The equilibrium vapor density ρ_{eq} appearing in (3) is, like the vapor pressure, a known function of the temperature of the bubble wall. The function $q(t)$ in eq. (4), which represents the accumulative effect of thermal radiation absorbed by the liquid, may be taken to be a linear function of time. Its effect is to initiate the growth of the equilibrium bubble (by raising the vapor pressure), but its influence is extremely transitory and the term will be neglected once the bubble growth has begun. It will be omitted from the equations of motion for the collapsing bubble. The parameters L, k and D $(= k/\rho c_v)$ appearing in (3) or (4) will be taken as constant, and equal to their values at the initial liquid temperature T_o.

The error incurred by the neglect of the variation of L, ρ, D, etc., with temperature is not significant in the case of the expanding bubble, because of the small temperature variation which occurs (essentially the initial superheat $T_o - T_b$). The error involved may be larger for the collapsing bubble, depending on the initial temperature and the initial bubble radius, but is not as serious in this case as the failure of the basic assumptions that the liquid is incompressible and that the bubble remains spherical. The trend of the physical quantities which describe the collapse of the vapor bubble is the same, whether L, D, etc., vary or not, however, and is given correctly by the analysis to follow.

In terms of the constants

$$\alpha = \sqrt{\frac{2\sigma}{\rho R_o^3}}, \qquad \zeta = \frac{L\rho_{eq}(T_o)R_o}{3k}\sqrt{\frac{\alpha D}{\pi}} \tag{5}$$

(which have the dimensions $\sec^{-1}$, °C respectively), we may define a set of dimensionless variables

$$\left.\begin{aligned} z &= \left(\frac{R}{R_o}\right)^3, \qquad u = \frac{\alpha}{R_o^4} \int_o^t R^4(y)\, dy, \\ \phi &= \frac{R_o}{2\sigma}\left[p_\infty - p_{eq}(T)\right], \qquad \xi = \frac{\rho_{eq}(T)}{\rho_{eq}(T_o)}, \end{aligned}\right\} \tag{6}$$

in terms of which the system of equations to be solved becomes

$$\frac{1}{6}\frac{d}{dz}\left[z^{7/3}\left(\frac{dz}{du}\right)^2\right] + \frac{1}{z^{1/3}} + \phi = 0, \tag{7}$$

$$\phi = \phi(T), \tag{8}$$

$$T = T_o + \frac{D}{k} q - \zeta \int_o^u \frac{\frac{d}{dv}(\xi z)\, dv}{\sqrt{u - v}}, \tag{9}$$

$$\xi = \xi(T). \tag{10}$$

The initial conditions for (7) are

$$z = 1, \qquad \frac{dz}{du} = 0, \qquad \text{at} \qquad u = 0. \tag{11}$$

The physical quantities we eventually wish to find are then given by

$$\left.\begin{aligned} t &= \frac{1}{\alpha}\int_o^u \frac{dv}{z^{4/3}(v)}, \\ R(t) &= R_o\, z^{1/3}, \\ \dot{R} &= \frac{\alpha R_o}{3}\, z^{2/3}\, \frac{dz}{du}, \\ \text{and} \quad T &= T_o + \frac{D}{k} q - \zeta \int_o^u \frac{\frac{d}{dv}(\xi z)\, dv}{\sqrt{u - v}}. \end{aligned}\right\} \tag{12}$$

The Expanding Vapor Bubble.

The pure vapor bubble which is to grow in a superheated liquid is assumed at some stage of the superheat to be in unstable equilibrium under the effects of surface tension, vapor pressure and external pressure. The bubble growth begins as a result of further superheating, which increases the vapor pressure and upsets the equilibrium. The condition for equilibrium at the time of release of the bubble $t = 0$ is that $\dot{R}(0) = R(0) = 0$, and hence by eq. (1) that

$$p_{eq}(T_o) - p_\infty = \frac{2\sigma}{R_o}. \tag{13}$$

Eq. (13) fixes the initial radius R_o of the bubble. As has been noted previously, the nucleus from which an actual bubble grows is not necessarily spherical, and its surface energy may be appreciably less than $4\pi\sigma R_o^2$; however, the nucleus from which an actual bubble grows and the free spherical vapor bubble of radius R_o are both in unstable equilibrium with respect to growth at the temperature T_o and external pressure p_∞. Table II (p. 65) gives a set of values of R_o for various superheat temperatures in water at an external pressure p_∞ of 1 atm. From the definition of $\phi(T)$, eq. (6), or the differential equation (7), the equilibrium condition (13) is equivalent to the condition

$$\phi(T_o) = -1. \tag{14}$$

As the bubble grows, the temperature at the bubble wall decreases toward the boiling point. Inasmuch as liquids will ordinarily support only a few degrees of superheat, the temperature variation involved in the growth is small, and an approximate expression for the dependence of vapor pressure on temperature will suffice. For $p_\infty = 1$ atm., a close fit to equilibrium vapor pressure data for water between 100°C and 110°C can be obtained by taking

$$\frac{p_{eq}(T) - p_\infty}{\rho} = A(T - T_b), \tag{15}$$

with $T_b = 100^\circ$C for water, and $A = 40{,}800$ c.g.s. units. By combining (15) with (5), (6), (9) and (13) or (14), one obtains for ϕ the relation

$$- \phi(T) = 1 + \frac{AD}{R_o^2 \alpha^2 k} q - \frac{A}{R_o^2 \alpha^2} \int_0^u \frac{\frac{d}{dv} (\xi z) dv}{\sqrt{u - v}} . \tag{16}$$

The term involving q in eq. (16) is extremely small, and therefore of importance only for a minute portion of bubble growth; it upsets the initial equilibrium. For a temperature rise of $1^{\circ}C/min$ in the liquid, this term is of order 10^{-8}, and it will be neglected once the bubble growth has begun. To fix the model, we shall take

$$\frac{D}{k} q(t) = at, \tag{17}$$

corresponding (see eq. (4)) to temperature rise of $1^{\circ}C$ in $\frac{1}{a}$ sec. in the liquid far from the bubble. Then from eq. (12),

$$\frac{AD}{R_o^2 \alpha^2 k} q(t) = \chi \int_0^u \frac{dv}{z^{4/3}(v)} , \tag{18}$$

where the constant

$$\chi = \frac{aA}{R_o^2 \alpha^3} . \tag{19}$$

In keeping with the above discussion, eq. (18) may be approximated by

$$\frac{AD}{R_o^2 \alpha^2 k} q(t) = \chi u. \tag{20}$$

Because of the small temperature range occurring for the expanding bubble, we shall further approximate ξ in eq. (16) by unity,* and write eq. (16) as

$$- \phi(T) = 1 + \chi u - \mu \int_0^u \frac{z'(v) dv}{\sqrt{u - v}} , \tag{21}$$

---

* The error involved here in setting $\xi = 1$ ($\rho_{eq}(T) = \rho_{eq}(T_o)$) may be estimated from the results given below for the temperature variation. It is found that the ratio $\frac{\xi'}{\xi} / \frac{z'}{z}$ remains less than 5 per cent at any time for the growing bubbles considered here. This ratio is identically the ratio of vapor velocity to liquid velocity at the bubble wall, which has been discussed previously.

where $z'(v) = \frac{dz}{dv}$ and

$$\mu = \frac{A\mathcal{L}}{R_o^2 \, a^2} . \tag{22}$$

The system of equations for the growing bubble thus simplifies to

$$\left.\begin{aligned} &\frac{1}{6}\frac{d}{dz}\left[z^{7/3} z'^2\right] = 1 - \frac{1}{z^{1/3}} + \chi u - \mu \int_0^u \frac{z' \, dv}{\sqrt{u-v}}, \\ &z' = 0, \qquad z = 1 \quad \text{at} \quad u = 0. \end{aligned}\right\} \tag{23}$$

A solution to eq. (23) will be found in four parts, corresponding to four (overlapping) phases of bubble growth, which may be labeled the "relaxation period", "early phase", "intermediate phase" and "asymptotic phase".

<u>Relaxation Period</u>.

Since the bubble growth starts from equilibrium, we shall put

$$z = e^w, \tag{24}$$

and assume that initially $w(u)$ and its derivatives are small. On neglecting the second or higher powers of $w, w', \ldots$, or products of such terms, one may rewrite eq. (23) in an approximate (linearized) form as

$$\left.\begin{aligned} &w''(u) - w(u) = 3\chi u - 3\mu \int_0^u \frac{w'(v) \, dv}{\sqrt{u-v}}, \\ &w(0) = w'(0) = 0. \end{aligned}\right\} \tag{25}$$

By putting $y(s) = \mathcal{L}[w]$ and taking the Laplace transform of (25) with respect to u, one obtains for $y(s)$ the equation

$$s^2 y(s) - y(s) = \frac{3\chi}{s^2} - 3\mu s y(s) \cdot \sqrt{\frac{\pi}{s}} ,$$

whence

$$y(s) = \frac{3\lambda}{s^2} \frac{1}{s^2 - 1 + 3\mu\sqrt{\pi s}} . \tag{26}$$

In order to match a later solution, we shall be mainly interested in the asymptotic form of the solution of (25) as $u \to \infty$, obtainable from the expansion of (26) about the singularities of $y(s)$. It is possible to obtain a solution to (25) in closed form by the means described below, and also to write a series expansion of $w(u)$ in powers of u from the Laurent expansion of (26) about $s = 0$, although these will not be used here.

The roots $\sqrt{s} = \sqrt{\beta}$, say, of

$$s^2 + 3\mu\sqrt{\pi s} - 1 = 0 \tag{27}$$

correspond to simple poles of $y(s)$. Eq. (26) may therefore be expanded in partial fractions using the factors indicated in (27). For a given root $\sqrt{s} = \sqrt{\beta}$, one obtains terms of the form

$$\frac{1}{s^2(\sqrt{s} - \sqrt{\beta})} = \frac{1}{\beta^2} \left[\frac{1}{\sqrt{s} - \sqrt{\beta}} - \frac{\beta^{3/2} + \beta s^{1/2} + s\beta^{1/2} + s^{3/2}}{s^2} \right] \tag{28}$$

multiplied by constant complex coefficients. By the use of the Laplace inversion integral it may be shown that

$$\mathcal{L}^{-1} \left[\frac{1}{\sqrt{s} - \sqrt{\beta}} \right] = \frac{1}{\sqrt{\pi u}} + \sqrt{\beta}\, e^{\beta u} [1 + \operatorname{erf}(\sqrt{\beta u})] \tag{29}$$

for all complex $\sqrt{\beta}$, and hence that for

$$\frac{\pi}{4} < |\arg \sqrt{\beta}| < \pi,$$

(29) vanishes as $u \to \infty$. It follows that the behavior of $w(u)$ as $u \to \infty$ is determined by those singularities of $y(s)$ for which

$$|\arg \sqrt{s}| < \frac{\pi}{4}. \tag{30}$$

Actually, there is but one root $\sqrt{s} = \sqrt{\beta}$ of (27) satisfying condition (30) for $0 < \mu < \infty$, and this root is real.

The residue of $y(s)$ at $s = \beta$ is given by

$$\frac{3\chi}{\beta^2} \quad \frac{1}{2\beta + \dfrac{3\mu\sqrt{\pi}}{2\sqrt{\beta}}},$$

or since β satisfies (27), by

$$\frac{3\chi}{\beta^2} \quad \frac{2\beta}{3\beta^2 + 1} \quad .$$

Hence as $s \to \beta$,

$$y(s) \sim \frac{6\chi}{\beta(3\beta^2 + 1)} \quad \frac{1}{s - \beta},$$

so, that as $u \to \infty$,

$$w(u) \sim \frac{6\chi}{\beta(3\beta^2 + 1)} \quad e^{\beta u}, \tag{31}$$

where, again, β in (31) is that root of eq. (27) satisfying condition (30). Alternatively, eq. (31) may be written

$$u \sim \frac{1}{\beta} \ln \left[\frac{\beta(3\beta^2 + 1)}{6\chi} \cdot w\right] \quad \text{as} \quad w \to \infty . \tag{32}$$

Since the transform

$$\mathcal{L}\,[T - T_\infty] = -\zeta\mathcal{L}\left[\int_0^u \frac{w'\,dv}{\sqrt{u - v}}\right] = -\zeta \quad \sqrt{\pi s} \quad y(s)$$

is asymptotic to $-\zeta\sqrt{\pi\beta}\; y(s)$ as $s \to \beta$, it follows that

$$T - T_\infty \sim -\zeta\sqrt{\pi\beta}\; w(u) \quad \text{as} \quad u \to \infty . \tag{33}$$

Moreover, to the degree of approximation used in the linearization,

$$\left.\begin{aligned} u &= \alpha t, \\ w &= 3\left(\frac{R}{R_o} - 1\right). \end{aligned}\right\} \tag{34}$$

From (31), (33) we thus obtain the relations

$$R \sim R_o \left[1 + \frac{2\chi}{\beta(3\beta^2+1)} e^{\alpha\beta t} \right], \tag{35}$$

$$T \sim T_c + at - 3\zeta \sqrt{\pi\beta} \left(\frac{R}{R_o} - 1\right). \tag{36}$$

By defining a time t_o by

$$\frac{2\chi}{\beta(3\beta^2+1)} = e^{-\alpha\beta t_o}, \tag{37}$$

one may write eq. (35) as

$$R \sim R_o [1 + e^{\alpha\beta(t-t_o)}]. \tag{38}$$

Thus the bubble radius remains practically equal to R_o until the time $t \approx t_c - \frac{1}{\alpha\beta}$ when it begins to increase, reaching $2R_o$ at about $t = t_o$. A tabulation of the significant parameters in eqs. (36), (38) for water at 1 atm. will be found in Table I, with the choice of $a = .01^\circ C/sec.$*

TABLE I.

Parameters of the Relaxation Period

T_c	R_o cm	t_o sec	$1/\alpha\beta$ sec	$3\zeta\sqrt{\pi\beta}$ °C	$.01\ t_o$ °C
102°C	1.56×10^{-3}	7.34×10^{-4}	5.05×10^{-5}	1.97	7.34×10^{-6}
104°C	$.75 \times 10^{-3}$	8.08×10^{-5}	4.48×10^{-6}	3.30	8.08×10^{-7}
106°C	$.48 \times 10^{-3}$	3.09×10^{-5}	1.56×10^{-6}	3.71	3.09×10^{-7}

* This choice for the parameter α corresponds roughly to the rate of the temperature rise observed by Dergarabedian[15] in his experiments on bubble growth in superheated water.

Because $1/\alpha\beta \ll t_o$, the bubble growth appears to start abruptly near $t = t_o$, rather than at the time of release, $t = 0$.

For given initial conditions T_o, p_∞, the duration

$$t_o = \frac{1}{\alpha\beta} \ln\left[\frac{\beta(3\beta^2+1)}{2\chi}\right] \tag{39}$$

of the relaxation period is completely determined by the heat source function $q(t)$, i.e. by the constant χ, upon which it depends logarithmically. However, it is evident from Table I that the heat source term (at) in eq. (36) becomes negligible in comparison with the other terms near the end of the relaxation period. From a physical standpoint, this means that at later times the bubble behavior is independent of the rate of increase of superheat which initiated the growth.

The asymptotic formulas for the linearized eq. (25) presented above are accurate over a range roughly defined by

$$u > \frac{1}{\alpha}, \qquad w \ll 1,$$

or

$$\frac{1}{\alpha\beta} < t < t_o - \frac{1}{\alpha\beta} .$$

Because of the smallness of χ, $w(u)$ increases over the range by a factor of several powers of 10 (about 10^6).

Early Phase.

In terms of $w = \ln z$ as independent variable, eq. (23) may be written

$$\frac{1}{6}\, e^{-w} \frac{d}{dw}\left[e^{\frac{13w}{3}} \left(\frac{du}{dw}\right)^{-2}\right] = 1 - e^{-\frac{w}{3}} - \mu \int_o^w \frac{e^v\, dv}{\sqrt{u(w) - u(v)}} \tag{40}$$

with the neglect of the heat source term. For small w, this reduces to

$$\frac{1}{6}\frac{d}{dw}\left(\frac{du}{dw}\right)^{-2} \approx \frac{w}{3} - \mu \int_o^w \frac{dv}{\sqrt{u(w) - u(v)}},$$

which is satisfied by

$$u = \frac{1}{\nu} \ln(Kw) \tag{41}$$

for arbitrary K, provided that

$$\nu^2 = 1 - 3\mu\sqrt{\nu} \int_0^1 \frac{dv}{\sqrt{\ln \frac{1}{v}}} . \tag{42}$$

Since the integral has the value $\sqrt{\pi}$, eq. (42) is identical with eq. (27). From the discussion of the relaxation period, it is clear that of the various roots of (42), the one to be chosen is that one which satisfies condition (30), $\nu = \beta$. In order to match the previous solution, eq. (32), we must further set

$$K = \frac{\beta(3\beta^2 + 1)}{6\chi} \tag{43}$$

in (41).

It is apparent from (41) that the derivative $\frac{du}{dw}$ of the solution $u(w)$ of (40) has a simple pole at $w = 0$, which suggests a solution of the form

$$\frac{du}{dw} = \frac{1}{\beta w} \left[1 + a_1 w + a_2 w^2 + \cdots \right], \tag{44}$$

or

$$u = \frac{1}{\beta} \ln \left[\frac{\beta(3\beta^2 + 1)}{6\chi} \cdot w \right] + \frac{a_1}{\beta} w + \frac{a_2}{2\beta} w^2 + \cdots . \tag{45}$$

By substituting (44) into the integral of (40), one obtains*

$$\mu \int_0^w \frac{e^v \, dv}{\sqrt{u(w) - u(v)}} = \mu w \sqrt{\pi\beta} \Big\{ 1 + \frac{w}{2} [2^{1/2} + 2(1 - 2^{1/2}) a_1]$$
$$+ \frac{w^2}{6} [3^{1/2} + 6(2^{1/2} - 3^{1/2}) a_1 + 3(1 - 2 \cdot 2^{3/2} + 3^{3/2}) a_1^2 + 3(1 - 3^{1/2}) a_2] + \cdots \Big\} . \tag{46}$$

By eq. (40), this must equal

$$1 - e^{-w/3} - \frac{1}{6} e^{-w} \frac{d}{dw}\left[e^{13w/3} \left(\frac{du}{dw}\right)^{-2}\right] = \frac{w}{3} (1 - \beta^2) - \frac{w^2}{6} \left[\frac{1}{3} + \beta^2(11 - 6a_1)\right]$$
$$+ \frac{w^3}{27} \left[\frac{1}{6} - \beta^2(115 - 129a_1 + 54a_1^2 - 36a_2)\right] + \cdots . \tag{47}$$

* See Appendix C for the evaluation of the integral.

The parameters $a_1, a_2, \ldots$ are then found by equating the coefficients of corresponding powers of w in (46), (47). A tabulation of the first seven of these, for varying superheats, will be found in Table II for the case of water at 1 atm. external pressure.

The time corresponding to (45) becomes

$$t = \frac{1}{\alpha} \int_0^w e^{-4v/3} u'(v)\, dv$$

$$= \frac{1}{\alpha\beta} \left\{ \ln \left[\frac{\beta(3\beta^2+1)}{6\chi} \cdot w \right] + (a_1 - \tfrac{4}{3})\, w \right.$$

$$\left. + (a_2 - \tfrac{4}{3} a_1 + \tfrac{8}{9}) \frac{w^2}{2} + \cdots \right\}, \tag{48}$$

the logarithmic term having been chosen to match eqs. (32), (34). The temperature may be found from eq. (46).

Asymptotic Phase.

During the early phase of bubble growth, characterized by the relaxation of surface tension, there is a rapid rise in the radial velocity $\dot{R}$ of the bubble wall until the cooling effect of evaporation becomes important. The rate of bubble growth thereafter is controlled by a balance between the rate of evaporation and the rate of cooling it produces.* Thus, while the vapor cavity grows by evaporation (since the vapor velocity is negligible), the motion of the liquid is caused by the difference between internal and external pressure. However, an increase in the evaporation rate tends to decrease the pressure difference.

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* The effects of liquid inertia are important in determining the bubble growth near the time of maximum radial acceleration. In the asymptotic phase of bubble growth, however, the inertial term

$$\frac{1}{6} \frac{d}{dz} (z^{7/3} z'^2)$$

in the differential equation is of smaller order than the surface tension term $\frac{1}{z^{1/3}}$. This point will be returned to below.

TABLE II

Parameters of the Early Phase of Vapor Bubble Growth

T_o °C	102	103	104	105	106
$R_o \times 10^3$ cm	1.558	1.019	.7507	.5901	.4832
$\alpha \times 10^5$ sec^{-1}	1.797	3.391	5.356	7.677	1.035
ζ °C	1.120	1.023	.9628	.9205	.8880
μ	.5598	.3411	.2407	.1841	.1480
β	.1101	.2632	.4168	.5340	.6177
a_1	2.0915	2.0322	1.9763	1.9456	1.9292
a_2	2.1577	2.0547	1.9463	1.8852	1.8526
a_3	1.4633	1.3761	1.2732	1.2129	1.1807
a_4	.7359	.6864	.6224	.5831	.5620
a_5	.2946	.2722	.2427	.2236	.2132
a_6	.09858	.08945	.07886	.07143	.06728
a_7	.02857	.02510	.02205	.01960	.01819

Now, it is clear that the bubble must continue to grow, since a stationary bubble is at the temperature of liquid superheat and therefore has a high internal pressure. Hence, the temperature at the bubble wall must continue to drop because of evaporation. But the temperature cannot drop below the boiling point and still maintain the pressure difference necessary for growth. It follows that the temperature of the bubble wall must approach a limit as $t \to \infty$, and this fact is sufficient to characterize the asymptotic phase of bubble growth.*

It is perhaps worthwhile to demonstrate at this point that the limiting temperature predicted by the mathematical model is what one would expect on physical grounds - the boiling temperature T_b of the liquid at the external pressure, for the sake of consistency and to justify statements made in section III above. The differential equation, with the neglect of the heat source term, may be written

$$\mu \int_0^u \frac{z'(v)\, dv}{\sqrt{u - v}} \sim 1 - \frac{1}{z^{1/3}} - \frac{1}{6}\frac{d}{dz}\,[z^{7/3}\, z'^2]. \tag{49}$$

If the last term on the right (the inertial term**) tends to vanish as $u \to \infty$, $z \to \infty$, then the limiting value of the temperature integral on the left side of eq. (49) is unity:

$$\mu \int_0^u \frac{z'\, dv}{\sqrt{u - v}} \sim 1 \qquad \text{as} \qquad u \to \infty . \tag{50}$$

The actual temperature is given by

$$T = T_o - \zeta \int_0^u \frac{z'\, dv}{\sqrt{u - v}} ,$$

so that by (50),

$$T_o - T \sim \frac{\zeta}{\mu} \qquad \text{as} \qquad u \to \infty . \tag{51}$$

---

* The slow temperature rise due to irradiation is here neglected.

** The kinetic energy of the liquid is given by

$$\int_R^\infty \left(\tfrac{1}{2}\rho v^2\right) \cdot 4\pi r^2\, dr = \left(\tfrac{2\pi}{9}\rho\, \alpha^2 R_o^5\right) z^{7/3}\, z'^2 .$$

According to the definitions (22) and (5),

$$\frac{\zeta}{\mu} = \frac{R_o^2\ \alpha^2}{A} = \frac{2\sigma}{\rho R_o A} ,$$

and so from the definition (13) of R_o,

$$\frac{\zeta}{\mu} = \frac{1}{A}\ [\frac{p_{eq}(T_o) - p_\infty}{\rho}] .$$

By eq. (15), this states that

$$\frac{\zeta}{\mu} = T_o - T_b$$

(ρ being considered a constant), and therefore, by comparison with eq. (51),

$$T \sim T_b \qquad \text{as} \qquad u \to \infty . \tag{52}$$

The conclusion (52) depends on the equation of motion only to the extent that it follows from the asymptotic vanishing of the inertial term. One can easily show, however, that the inertial term must vanish whether (52) holds or not, provided only that the temperature approaches some limit as $u \to \infty$. For this implies that

$$\int_o^u \frac{z'\ dv}{\sqrt{u - v}} \sim \text{const.} \qquad \text{as} \qquad u \to \infty . \tag{53}$$

Multiplication of (53) by $\dfrac{1}{\sqrt{x - u}}$ and integration from $u = 0$ to x yields, after a change in the order of integration,

$$\int_o^x \frac{du}{\sqrt{x - u}} \int_o^u \frac{z'(v)\ dv}{\sqrt{u - v}} = \int_o^x z'(v)\ dv \int_v^x \frac{du}{\sqrt{x - u}\ \sqrt{u - v}}$$

$$= \pi[z(x) - 1], \qquad \sim \text{const.} \cdot 2\sqrt{x} \tag{54}$$

The vanishing of the inertial term in (49) then follows from eq. (54), which shows in fact that the inertial term is of a smaller order of magnitude in the asymptotic range than the surface tension term $z^{-1/3}$. The constant in (54) is $1/\mu$ according to eq. (50), so that eq. (54) yields

$$z(u) \sim \frac{2}{\pi\mu}\sqrt{u} \qquad \text{as} \qquad u \to \infty . \tag{55}$$

Eq. (55) describes the asymptotic bubble growth, but is not yet useful, since it provides no means of matching the indicated asymptotic solution of eq. (49) with earlier solutions. The possibility of matching solutions depends on the possibility of shifting the asymptotic solution in t (or in u) so as to account for the relaxation period of bubble growth. It is necessary that one be free to shift the asymptotic solution since the duration of the relaxation period depends completely on the choice of the heat source term, while the subsequent behavior of the bubble is independent of this term.

The means for making an arbitrary time shift is furnished by noting that, in addition to the asymptotic form of solution (55), eq. (49) also possesses the solution $z(u) \equiv 1$. Thus the complete asymptotic solution may be described by

$$\left.\begin{aligned} &z(u) = 1, && 0 < u \leq u_1, \\ &\mu \int_0^u \frac{z'(v)\,dv}{\sqrt{u-v}} = 1 - \frac{1}{z^{1/3}} - \frac{1}{6z'}\frac{d}{du}\left[z^{7/3} z'^2\right], && u > u_1. \end{aligned}\right\} \tag{56}$$

From eq. (12), the time corresponding to eqs. (56) becomes

$$t = \frac{1}{\alpha}\int_0^u \frac{dv}{z^{4/3}(v)} = \begin{cases} \dfrac{u}{\alpha}, & 0 < u \leq u_1, \\[2ex] \dfrac{u_1}{\alpha} + \dfrac{1}{\alpha}\displaystyle\int_{u_1}^u \frac{dv}{z^{4/3}}, & u > u_1, \end{cases} \tag{57}$$

so that u_1/α here represents the duration of the relaxation period. The time shift may be introduced explicitly into the asymptotic solution by using the fact that if $z(u)$ is a solution of eq. (56), $z(u + u_o)$ is also a solution, with delay period $(u_1 - u_o)/\alpha$.

A consistent scheme for continuing the asymptotic solution may be found by taking the solution to be of the form

$$\left.\begin{aligned} &z(u) = 1, \qquad 0 < u \leq u_1, \\ &z(u) \sim \frac{2}{\pi\mu}\sqrt{u-u_o}\left\{1 + \frac{b_1}{(u-u_o)^{1/6}} + \cdots + \frac{b_5}{(u-u_o)^{5/6}} + \frac{b_6 \ln(u-u_o)}{u-u_o}\right\}, \qquad u > u_1, \end{aligned}\right\} \tag{58}$$

to seven terms, where u_o is a constant.* When the coefficients b_k have been determined, the difference $(u_1 - u_o)$ is fixed by the requirement $z(u_1) = 1$. The matching with earlier solutions is then accomplished by adjusting u_o.**

When (58) is substituted into the integral of (56) the result is+

$$\mu \int_{u_1}^{u} \frac{z'(v)\, dv}{\sqrt{u - v}} \sim 1 + .89266 \frac{b_1}{(u-u_o)^{1/6}} + .77306 \frac{b_2}{(u-u_o)^{2/6}}$$

$$+ \left(\frac{2}{\pi} b_3 - \mu\right) \frac{1}{(u-u_o)^{3/6}} + .47545 \frac{b_4}{(u-u_o)^{4/6}}$$

$$+ .27450 \frac{b_5}{(u-u_o)^{5/6}} + 2 \frac{b_6}{u - u_o} \quad . \tag{59}$$

By eq. (56), the expression (59) is also asymptotic to

$$1 - \frac{1}{z^{1/3}} - \frac{1}{6z'} \frac{d}{du} [z^{7/3} z'^2]. \tag{60}$$

This may be expanded by (58) to give, on equating coefficients of corresponding powers of $(u-u_o)$ in (59), (60), a set of successive equations for the parameters $b_1, \ldots, b_6$. At each step one has (as for the early phase coefficients) a linear equation for the unknown parameter. A tabulation of these parameters for various superheat temperatures in water at an external pressure of 1 atm. is given in Table III.

The leading terms in the asymptotic solution are

$$z = (R/R_o)^3 \sim \frac{2}{\pi\mu} \sqrt{u} \left\{1 + O(u^{-1/6})\right\} ,$$

$$t \sim \frac{3}{\alpha} \left(\frac{\pi\mu}{2}\right)^{4/3} u^{1/3} \left\{1 + O(u^{-1/6})\right\} ,$$

$$T - T_o \sim \frac{\alpha^2 R_o^2}{A} \left\{1 + O(u^{-1/6})\right\} .$$

---

* Higher terms are of the form $[\ln(u-u_o)]^n/(u-u_o)^{k/6}$, where n and k are integers.

** The match is better obtained in practice by shifting the asymptotic $R(t)$ curves.

\+ See Appendix D for the evaluation of the integral.

TABLE III

Parameters of the Asymptotic Phase of Vapor Bubble Growth.

T_o °C	102	103	104	105	106
$R_o \times 10^3$ cm	1.558	1.019	.7507	.5901	.4832
$\alpha \times 10^{-5}$ sec^{-1}	1.797	3.391	5.356	7.677	1.035
ζ °C	1.120	1.023	.9628	.9205	.8880
μ	.5598	.3411	.2407	.1841	.1480
b_1	-1.073	- .9099	- .8101	- .7409	- .6890
b_2	- .4709	- .4624	- .7122	-1.334	-2.506
b_3	- .2339	-1.481	- .3586	- .9725	-1.972
b_4	- .5534	1.258	- .1970	-4.598	-2.510
b_5	-1.775	3.064	4.298	18.50	65.84
b_6	- .7423	- .2670	.6166	- .4736	-48.65

Thus

$$\left.\begin{aligned} R &\sim R_o\left(\frac{2}{\pi\mu}\right)\sqrt{\frac{\alpha t}{3}}\left\{1 + O(t^{-1/2})\right\} , \\ T - T_o &\sim -\frac{\alpha^2 R_o^2}{A}\left\{1 + O(t^{-1/2})\right\} ; \end{aligned}\right\} \qquad (61)$$

or in terms of the original physical constants,

$$\left.\begin{aligned} R &\sim 2\sqrt{\frac{3}{\pi}}\ \frac{k(T_o - T_b)}{L\rho_{eq}(T_o)\ \sqrt{D}}\ t^{1/2}\left\{1 + O(t^{-1/2})\right\} , \\ T - T_o &\sim (T_b - T_o)\left\{1 + O(t^{-1/2})\right\} . \end{aligned}\right\} \qquad (62)$$

The asymptotic temperature relation has been discussed previously. The radius relation has also a simple physical interpretation, which may be given here. By differentiating the first of equations (62), one obtains

$$\dot{R} \sim \sqrt{\frac{3}{\pi}} \cdot k\,\frac{(T_o - T_b)}{\sqrt{Dt}} \cdot \frac{1}{L\rho_{eq}(T_o)} ,$$

which may also be written as

$$4\pi R^2 \cdot k\left(\frac{T_o - T_b}{\sqrt{\frac{\pi}{3}\ Dt}}\right) \sim L\rho_{eq}(T_o)\,\frac{d}{dt}\left(\frac{4}{3}\,\pi R^3\right).$$

In this form, one may readily recognize the heat transfer relation holding at the bubble wall, the right side giving the heat gain in the vapor and the left side giving the heat loss from the liquid. The temperature gradient is here expressed in terms of the ratio of the temperature drop occurring asymptotically at the bubble wall to the thickness of the thermal boundary layer in which it occurs. The particular choice $\sqrt{\frac{\pi}{3}\,Dt}$ for the characteristic diffusion length could not, of course, have been predicted beforehand.

While the leading terms of the asymptotic expansions given in (62) show the essential variation of the physical quantities which describe the bubble growth, they are of limited usefulness, and may be in error by as much as 40 per cent (depending on the superheat) while the bubble radius is still small. More accurate expressions may be found by carrying out the time integration indicated in eq. (57) and substituting in the coefficients from Table III. The result of such calculations is presented in Fig. 3, which follows the asymptotic solutions down to a radius of 4×10^{-3} cm for the indicated superheats in water at 1 atm. external pressure. Inasmuch as the duration of the relaxation period may be chosen arbitrarily so far as these asymptotic solutions are concerned, the time scale is determined only to within an arbitrary additive constant (the constant u_1/α mentioned above) which may vary from one curve to another. The actual spacing of the curves as presented was chosen so that the time intercepts at $R = .004$ cm were equally spaced.

The experimental evidence available thus far covers only the asymptotic range of bubble growth. Observations on the growth of vapor bubbles in water have been made by Dergarabedian,[15] and are presented in Figs. 4,5,6, together with the theoretical predictions. The theoretical curves were obtained by graphical interpolation from the set of curves plotted in Fig. 3. The time origins for both the theoretical curves and the experimental points are arbitrary, so that a time translation of the theoretical curve has been made in each case to give the best fit. The agreement is seen, however, to be very good.

The importance of the heat transfer at the bubble wall is shown in Fig. 4, where the theoretical curve obtained with the neglect of this effect is also plotted.* The asymptotic form of this solution is readily obtained from eq. (1) by setting $p_{eq}(T) = p_{eq}(T_o)$ there. The differential equation may be written

$$\frac{1}{2R^2 \dot{R}} \frac{d}{dt} [R^3 \dot{R}^2] = \frac{2\sigma}{\rho R_o} (1 - \frac{R_o}{R})$$

with the help of the definition (13), and yields on integration from R_o to R, $\dot{R}_o$ to $\dot{R}$,

$$\dot{R}^2 = \dot{R}_o^2 \left(\frac{R_o^3}{R^3} \right) + \frac{4\sigma}{3\rho R_o} \left(1 - \frac{R_o^3}{R^3}\right) - \frac{2\sigma}{\rho R} \left(1 - \frac{R_o^2}{R^2}\right).$$

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* The solution for the motion of a bubble under constant vapor pressure conditions was given by Rayleigh[16] and applied by him to the case of a collapsing bubble.

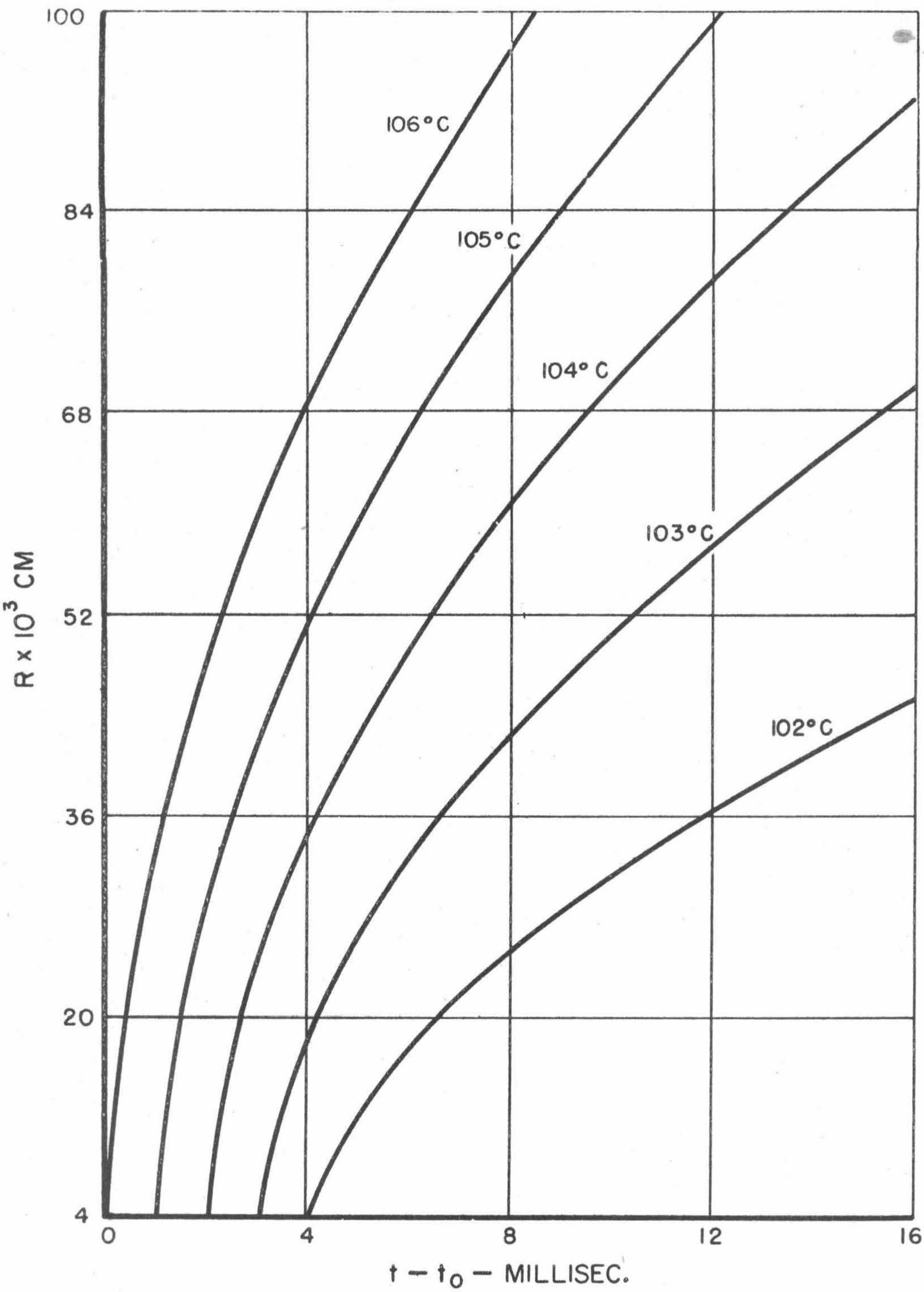

Fig. 3 - Asymptotic radius versus time curves calculated for water at 1 atm. external pressure and the indicated superheat temperature.

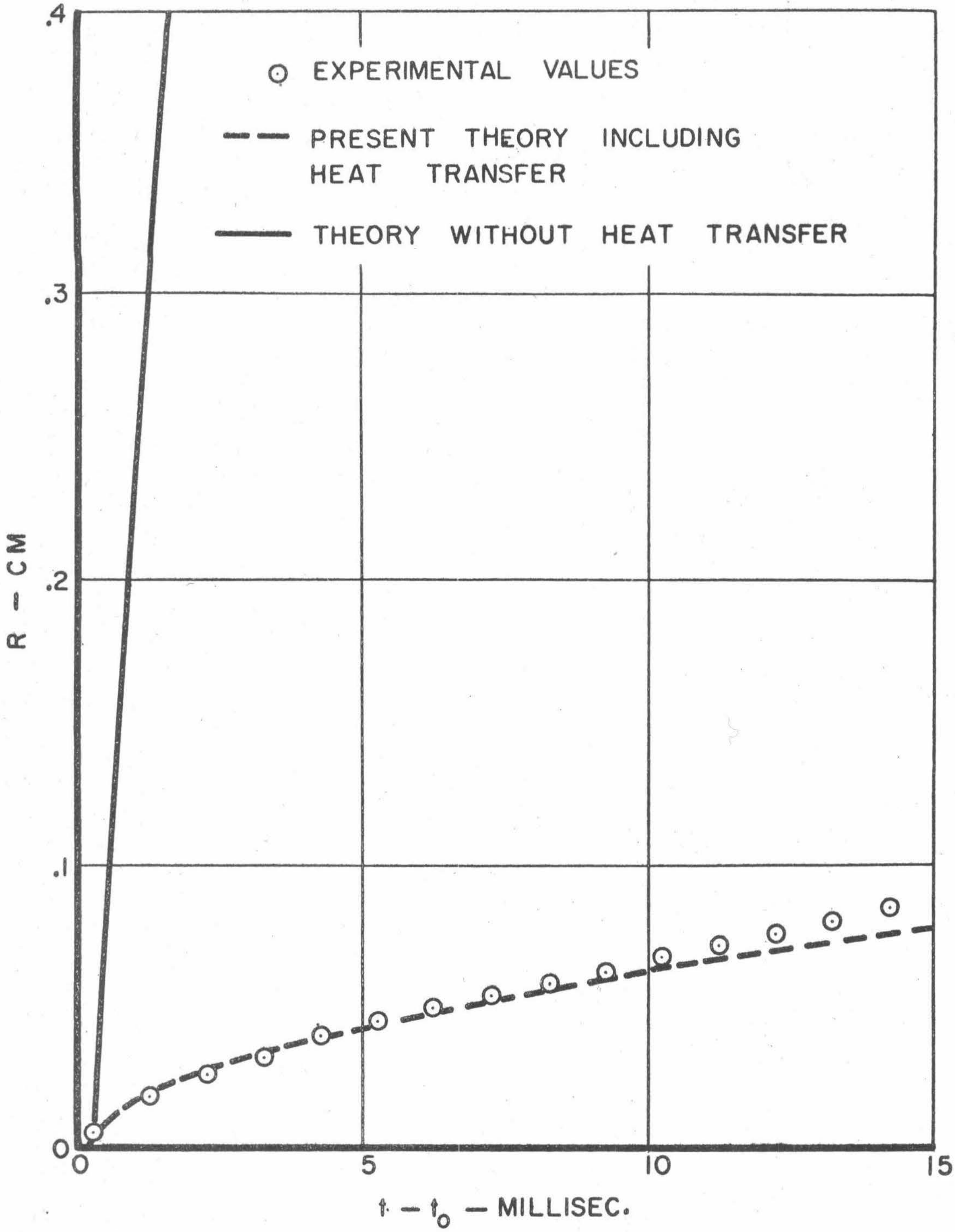

Fig. 4 - Comparison of theoretical bubble radius-time values with experimental values for water at 1 atm. external pressure, superheated to 103.1°C. The solid curve is the Rayleigh growth curve, obtained by neglecting heat transfer effects; the dashed curve is that predicted by the asymptotic solution of the text, which takes heat transfer into account.

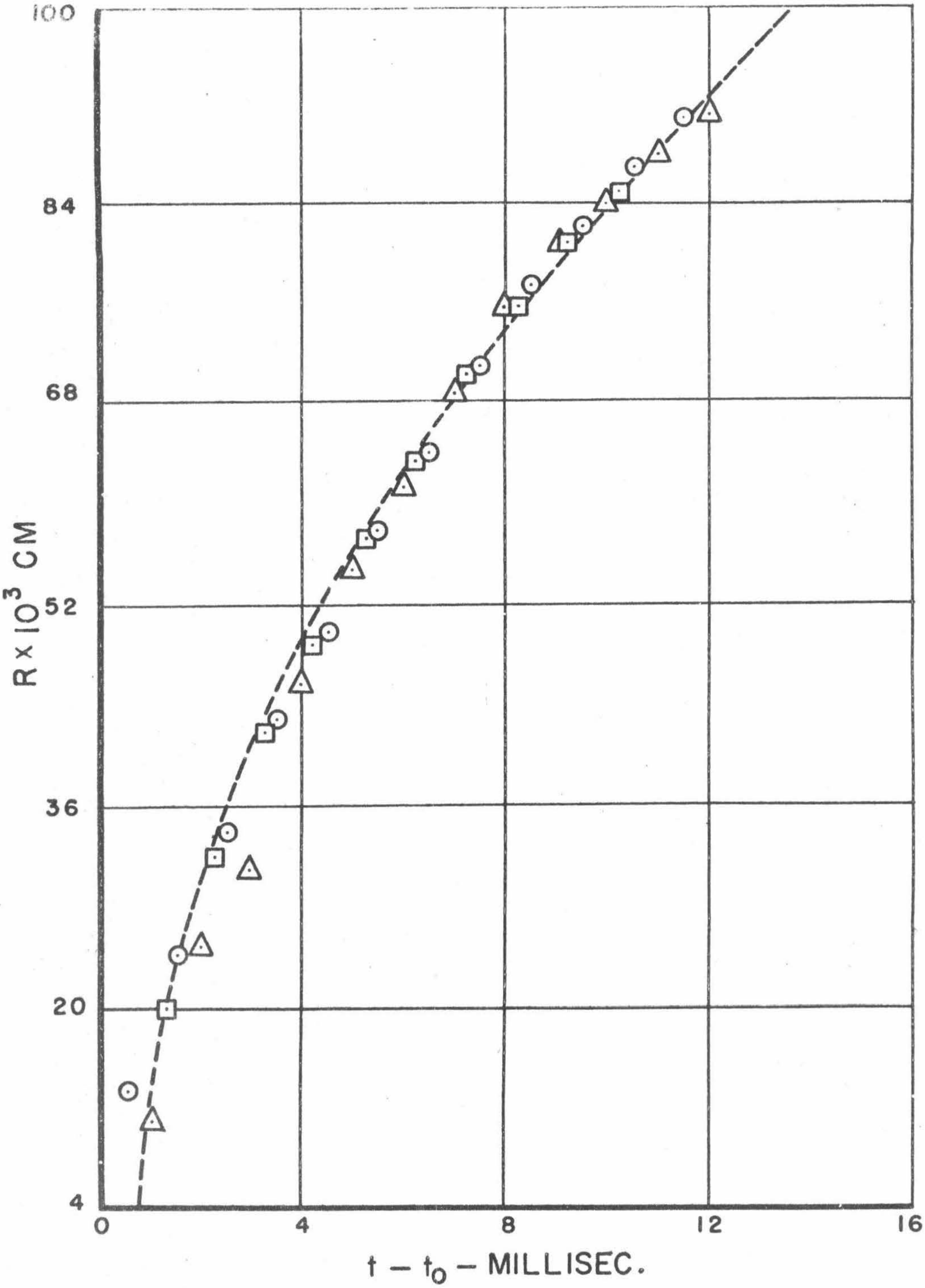

Fig. 5 - Comparison of theoretical radius-time values with three sets of experimental values obtained in water at 1 atm. external pressure, superheated to 104.5°C.

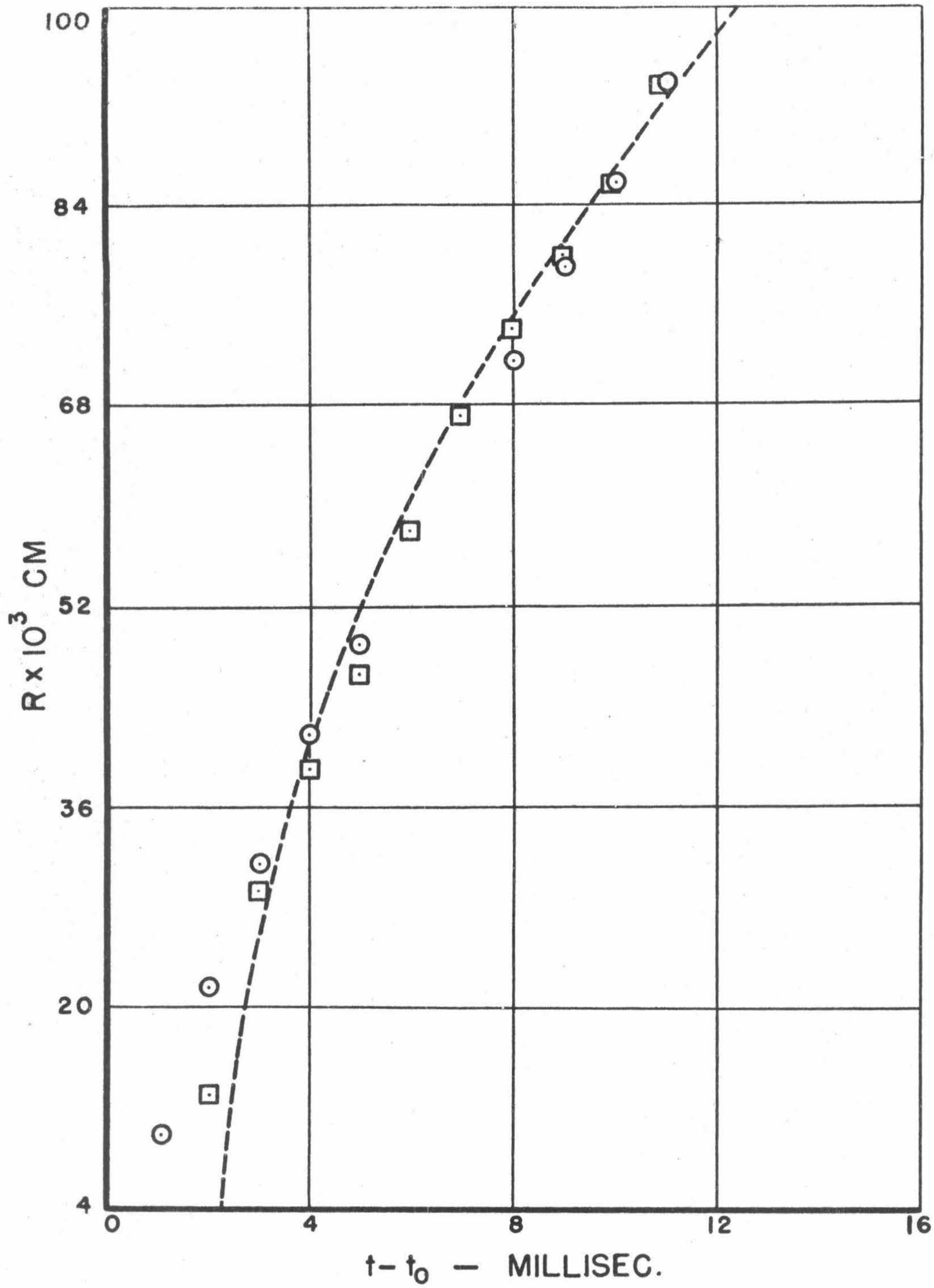

Fig. 6 - Comparison of theoretical radius-time values with two sets of experimental values obtained for water at 1 atm. external pressure, superheated to 105.3°C.

As $R \to \infty$, this gives

$$\dot{R} \sim \sqrt{\frac{4\sigma}{3\rho R_o}} = R_o\, \alpha\sqrt{\frac{2}{3}}\,,$$

which is a constant.

Experiments have recently been performed by Dergarabedian on vapor bubble growth in pure CCl_4. If the rates of bubble growth in this liquid are compared with those of water at the same value of the temperature difference $(T_o - T_b)$ and at comparable times, they should be about in the same ratio as $k/L\rho_{eq}\, D^{1/2}$ for the two liquids. This constant is 3.5 times greater in water than in carbon tetrachloride. Dergarabedian's observations on bubble growths are in good agreement with this value.

Intermediate Solution.

The early phase and asymptotic solutions presented above join in the neighborhood of the maximum value of dz/du. While the match of these solutions is fairly good for all superheats, it is nevertheless desirable to have available a solution which covers the critical region, to facilitate the matching process.

The intermediate solution presented here will be an expansion about the point $u = u_i$ defined by

$$z''(u_i) = 0. \tag{63}$$

Since the early phase solution is not assumed to be accurate at this point, the actual value of u_i or $z(u_i)$ is unknown. In order to determine these quantities, we require that the intermediate solution and its derivative shall coincide with values obtained from the early phase solution at a point $u = u_e$ where that solution is accurate. The expansion about the inflection point u_i is constructed as follows:*

---

* The difficulties which arise for any such intermediate solution are connected with the expansion of the convolution integral in the differential equation. Thus, a solution about a known point (such as u_e) which assumes the integral and all of its derivatives to be known does not actually make use of the information given by the differential equation, while a solution about a known point which uses the minimum of data necessary (the value of z and z', say, at the point of expansion) involves about the same procedure as that given below.

Assume that $z(u)$ has an expansion about u_i

$$\left.\begin{aligned} z(u_i + x) &= Z[1 + c_1 x + c_3 \frac{x^3}{6} + \cdots] \qquad (Z \equiv z(u_i)), \\ \text{so that} \qquad & \\ z'(u_i + x) &= Z[c_1 + c_3 \frac{x^2}{2} + \cdots], \\ z''(u_i + x) &= Z[c_3 x + \cdots]. \end{aligned}\right\} \tag{64}$$

The expansions (64) are to be substituted into the differential equation (with the heat source term omitted)

$$zz'' + \frac{7}{6} z'^2 = \frac{3}{z^{4/3}} \left[1 - \frac{1}{z^{1/3}} - \mu \int_o^u \frac{z'(v)\, dv}{\sqrt{u - v}} \right]. \tag{65}$$

Now, the integral in (65), evaluated at $u + x$, is

$$\begin{aligned} \int_o^{u+x} \frac{z'(v)\, dv}{\sqrt{u + x - v}} &= \int_o^x \frac{z'(v)\, dv}{\sqrt{u + x - v}} + \int_x^{u+x} \frac{z'(v)\, dv}{\sqrt{u + x - v}} \\ &= \int_o^x \frac{z'(v)\, dv}{\sqrt{u + x - v}} + \int_o^u z'(u + x - v) \frac{dv}{\sqrt{v}} \\ &= \int_o^x \frac{z'(v) dv}{\sqrt{u + x - v}} + \sum_{k=o}^{\infty} \frac{x^k}{k!} \int_o^u z^{(k+1)} (u - v) \frac{dv}{\sqrt{v}}, \end{aligned} \tag{66}$$

valid for sufficiently small x. But for small x, $z'(x) \approx 0$, so that when (66) is valid, the first integral in (66) is negligible. Thus for $u = u_i$,

$$\int_o^{u_i + x} \frac{z'(v) dv}{\sqrt{u_i + x - v}} \approx I_o + I_1 x + I_2 \frac{x^2}{2!} + \cdots, \tag{67}$$

say, where

$$I_k = \int_o^{u_i} \frac{z^{(k+1)}(v)\, dv}{\sqrt{u_i - v}}. \tag{68}$$

If u_i were known, we could use (67) in eq. (65) to obtain, on equating coefficients of corresponding powers of x in (65), a set of relations

$$\left.\begin{aligned} \frac{7}{6} c_1^2 &= \frac{3}{z^{10/3}} \left[1 - \frac{1}{z^{1/3}} - \mu I_o\right], \\ c_3 &= \frac{1}{z^{10/3}} \left[\left(-4 + \frac{5}{z^{1/3}}\right) c_1 - \mu (3I_1 - 4c_1 I_o)\right], \ \ldots , \end{aligned}\right\} \qquad (69)$$

to solve for the parameters $c_1, c_3, \ldots$. However, the I_k are not yet determined.

Since the solution to (65) is assumed known for $u \leq u_e$, $u_e < u_i$, let

$$J_k = \int_o^{u_e} \frac{z^{(k+1)}(v)\, dv}{\sqrt{u_i - v}} \ , \qquad (70)$$

$$L_k = \int_{u_e}^{u_i} \frac{z^{(k+1)}(v)\, dv}{\sqrt{u_i - v}} \ , \qquad (71)$$

so that

$$I_k = J_k + L_k \qquad (72)$$

in (68), and set

$$\delta = u_i - u_e, \qquad \varepsilon = u_i - v \qquad (73)$$

in the integrals. Then in L_o, for instance,

$$z'(v) = z'(u_i - \varepsilon) = Z(c_1 + \tfrac{1}{2} c_3 \varepsilon^2 + \cdots),$$

giving

$$L_o = \int_{u_i}^{u_e} \frac{z'(v)\, dv}{\sqrt{u_i - v}} = 2Z\sqrt{\delta}\ (c_1 + \tfrac{1}{10} c_3 \delta^2 + \cdots) .$$

Thus

$$I_o = J_o(\delta) + 2Z\sqrt{\delta}\ (c_1 + \tfrac{1}{10} c_3 \delta^2 + \cdots),$$

and similarly

$$I_1 = J_1(\delta) + 2Z\sqrt{\delta}\ (-\tfrac{1}{3} c_3 \delta + \cdots), \ \ldots \qquad (74)$$

may be found if Z, c_1, c_3, ... , and δ are known. The feasibility of this procedure depends on the fact that a good estimate of δ is already available from the early phase solution, and that the

$$J_k(\delta) = \int_0^{u_e} \frac{z^{(k+1)}(v)\, dv}{\sqrt{u_e + \delta - v}}$$

are slowly varying functions of δ. This follows from the relation

$$\frac{d}{d\delta} J_k(\delta) = J_{k+1}(\delta) - \frac{z^{(k+1)}(u_e)}{\sqrt{\delta}} \quad , \tag{75}$$

since in the early phase $z^{(k+1)} \ll z^{(k)}$.

Assuming that the contributions to I_0, I_1 from higher powers of δ than those written in (74) may be neglected, we terminate the expansions as written and substitute them into (69). Together with the conditions

$$z(u_e) = Z(1 - c_1\delta - \frac{1}{6} c_3 \delta^3),$$

$$z'(u_e) = Z(c_1 + \frac{1}{2} c_3 \delta^2)$$

from (64), the equations (76)

$$\frac{7}{6} c_1^2 = \frac{3}{z^{10/3}} \left\{ 1 - \frac{1}{Z^{1/3}} - \mu [J_0(\delta) + 2Z\sqrt{\delta}\,(c_1 + \frac{1}{10} c_3 \delta^2)] \right\},$$

$$c_3 = \frac{1}{Z^{10/3}} \left\{ (-4 + \frac{5}{Z^{1/3}})\, c_1 - 3\mu [J_1(\delta) + 2Z\sqrt{\delta}\,(-\frac{1}{3} c_3 \delta)] + 4\mu c_1 [J_0(\delta) + 2Z\sqrt{\delta}\,(c_1 + \frac{1}{10} c_3 \delta^2)] \right\}$$

constitute a system of four simultaneous equations for the four unknowns Z, c_1, c_3, δ. Inasmuch as one and only one point of inflection of $z(u)$ is known to exist, these equations have a unique solution.

It should be noted that because of the definitions of u and z, the maximum radial velocity $\dot{R}$ of the bubble wall does not occur at the same value of u (or t) as the maximum value of $z'(u)$. The discrepancy is not great for small superheats, but for larger superheats the point defined by $\ddot{R} = 0$ moves onto the asymptotic end of the $z(u)$ curve.

Solution for the Expanding Bubble.

The results of the above theory for water at initial temperatures $T_o = 103, 106^\circ C$ and external pressure $p_\infty = 1$ atm. have been plotted in Figs. 7, 8, and 9, 10. The bubble was taken to be in equilibrium at time $t = 0$ when the heat source $q(t)$ is introduced; $q(t)$ was arbitrarily chosen to correspond to a temperature rise of $1^\circ C$ in 100 sec in the water far from the bubble.*

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* See the footnote on page 61.

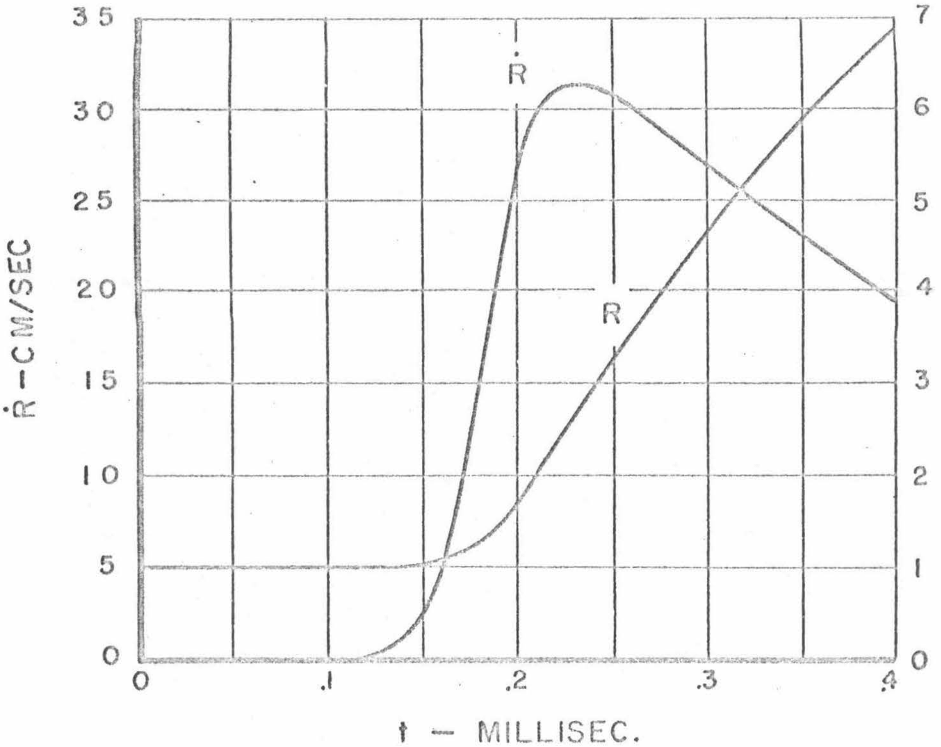

Fig. 7 - Theoretical radius and radial velocity curves for the growth of a pure vapor bubble in water at 1 atm external pressure, superheated to 103°C.

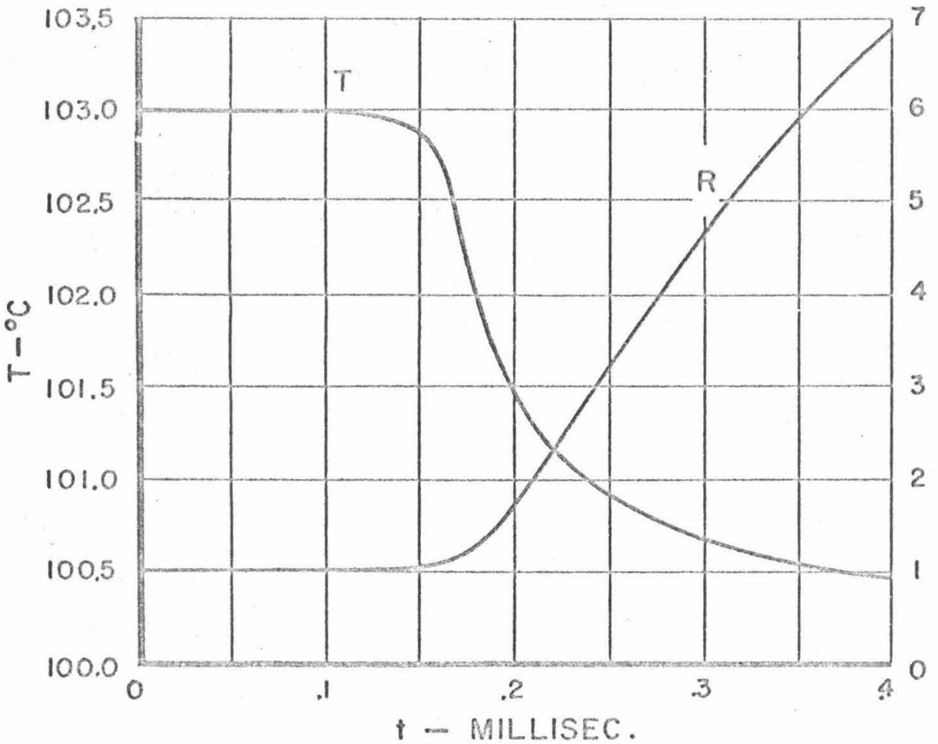

Fig. 8 - Theoretical radius and bubble wall temperature curves for the 103° vapor bubble of Fig. 7.

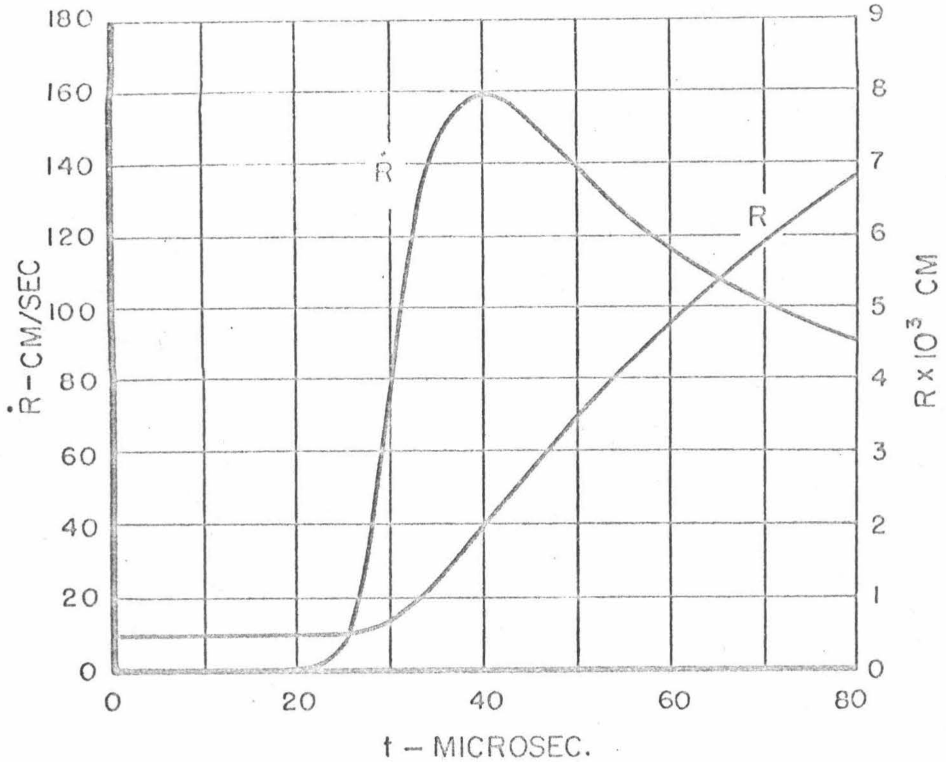

Fig. 9 - Theoretical radius and radial velocity curves for the growth of a pure vapor bubble in water at 1 atm. external pressure, superheated to 106°C.

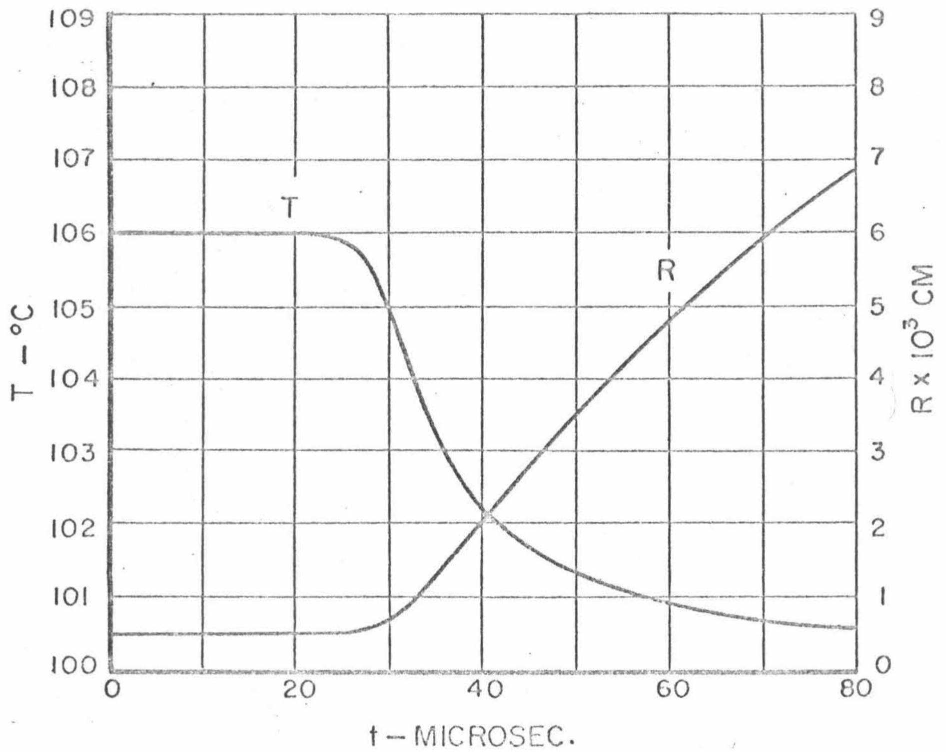

Fig. 10 - Theoretical radius and bubble wall temperature curves for the 106° vapor bubble of Fig. 9.

The Collapsing Vapor Bubble.

Because of the large temperature variations which occur when a vapor bubble collapses in water below the boiling temperature; a simple analytic expression for the vapor pressure or vapor density variations cannot be found. If we take our data from equilibrium vapor pressure and density tables, we commit the treatment of the problem to a numerical one from the beginning.

The system of equations to be solved, eqs. (7)-(11), is unchanged. In this case, however, the vapor pressure at the initial temperature T_o is less than the external pressure, and initial conditions of dynamic equilibrium cannot prevail for the pure vapor bubble. There is therefore no need to retain the heat source term in eq. (9), and we shall put $q(t) = 0$. We continue to assume that initially the vapor bubble and surrounding liquid are in thermal equilibrium at temperature T_o.

It is convenient to transform the temperature equation. By multiplying eq. (9) by $(x - u)^{-1/2}$ and integrating it from $u = 0$ to x, one obtains, after an integration by parts, the relation

$$\left.\begin{aligned} &\xi(u)\, z(u) - 1 = \frac{2}{\pi \zeta} \int_0^u \theta'(v) \sqrt{u - v}\; dv, \\ &\text{where} \\ &\theta = T - T_o. \end{aligned}\right\} \qquad (77)$$

The system of equations to be solved becomes

$$\left.\begin{aligned} &\frac{1}{6} \frac{d}{dz} [z^{7/3} z'^2] + \frac{1}{z^{1/3}} + \phi = 0, \\ &\phi = \phi(\theta), \\ &\xi z - 1 = \frac{2}{\pi \zeta} \int_0^u \theta' \sqrt{u - v}\; dv, \\ &\xi = \xi(\theta); \\ &z(0) = 1, \quad z'(0) = 0, \quad \theta(0) = 0. \end{aligned}\right\} \qquad (78)$$

The system (78) was solved numerically for initial temperature $T_o = 22^oC$, external pressure $p_\infty = .544$ atm., and initial bubble radius (which is undetermined for the non-equilibrium bubble) $R_o = .25$ cm. The method of solution is given in Appendix E. The particular initial data chosen here correspond to values which have been obtained experimentally.*

Although the temperature effects become significant during the collapse, the dynamics of the particular bubble considered here differs very little from that predicted by the Rayleigh solution of the problem(16) over most of the collapse. The Rayleigh solution, which neglects heat transfer effects, is readily obtainable from (78) under the assumption that ϕ stays constant, and equal to $\phi(T_o)$. The equation of motion is

$$\left.\begin{aligned} &\frac{1}{6}\frac{d}{dz}\left[z^{7/3}\, z'^2\right] + \frac{1}{z^{1/3}} + \phi_o = 0, \\ &z(0) = 1, \qquad z'(0) = 0, \end{aligned}\right\}$$

which yields

$$\frac{1}{6} z^{7/3}\, z'^2 = \phi_o(1 - z) + \frac{3}{2}\left(1 - z^{2/3}\right) \tag{79}$$

on integration. Since

$$\phi_o = \frac{R_o}{2\sigma}\left[p_\infty - p_{eq}(T_o)\right] \approx 2 \times 10^3$$

is much larger than 3/2, eq. (79) may be approximated by

$$\frac{1}{6} z^{7/3}\, z'^2 = \phi_o(1 - z),$$

or

$$z' = -\sqrt{6\phi_o} \cdot z^{-7/6}\sqrt{1 - z}\ ,$$

where the negative square root of z'^2 must be chosen to correspond to the collapsing bubble. From eq. (12),

$$\frac{dz}{dt} = \alpha\, z^{8/6}\, z' = -\alpha\sqrt{6\phi_o} \cdot z^{1/6}(1 - z)^{1/2},$$

which yields

$$t = \frac{1}{\alpha\sqrt{6\phi_o}}\int_z^1 \frac{x^{-1/6}\,dx}{\sqrt{1 - x}} = \frac{R_o\sqrt{\rho}}{\sqrt{6[p_\infty - p_{eq}(T_o)]}}\int_{(R/R_o)^3}^1 \frac{x^{-1/6}dx}{\sqrt{1 - x}} \tag{80}$$

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* The experiments, performed at the Hydrodynamics Laboratory of the California Institute of Technology, were reported by M.S. Plesset in ref. (13).

on integration. The time corresponding to the full system (78) was found by a numerical integration of the relation

$$t = \frac{1}{a} \int_0^u \frac{dv}{z^{4/3}(v)}$$

using the values of z obtained from the numerical solution of (78).

A comparison of the two solutions for the collapsing bubble is given in Fig. 11. The magnitude of the radial velocity of the bubble wall obtained from the numerical solution is plotted in Fig. 12, and the corresponding temperature at the bubble wall in Fig. 13. The numerical solution was not carried out farther than shown in Figs. 12 or 13, because of the breakdown of the assumptions underlying the theory presented here: the parameters L, ρ, D, etc. begin to vary significantly near the end of collapse, the liquid velocity becomes so large that compressibility effects may become important in the liquid, and the spherical bubble shape becomes unstable to small distorting influences.

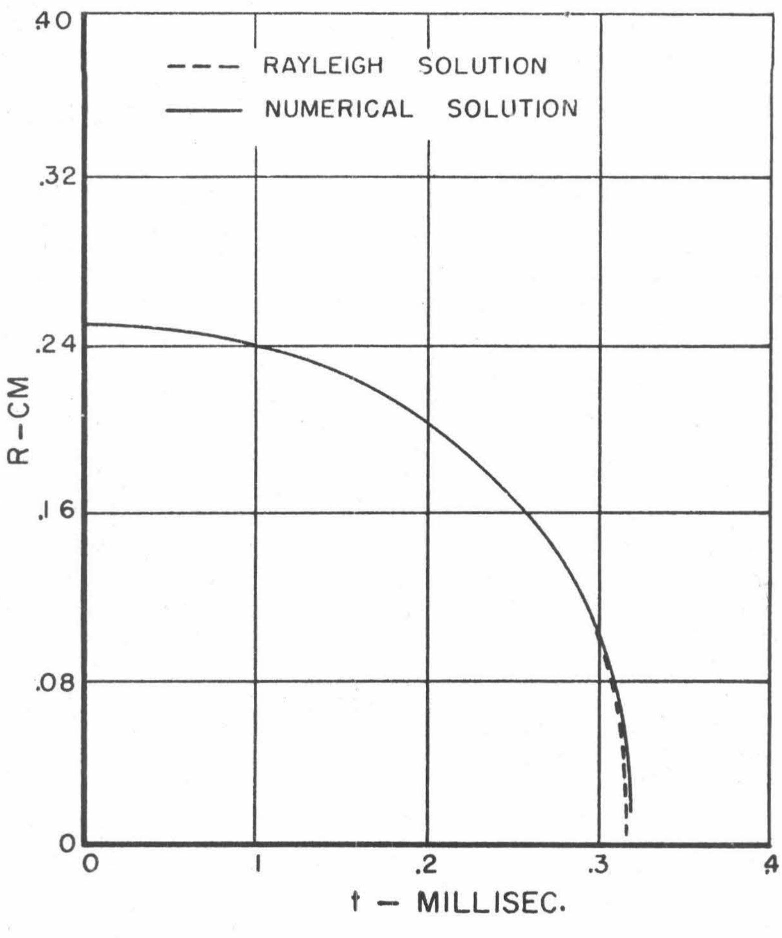

Fig. 11 - Comparison of the numerical solution of the text (which includes heat transfer effects) with the Rayleigh solution (which neglects heat transfer effects) for a vapor bubble of initial radius .25 cm, collapsing in water at 22°C and an external pressure .544 atm.

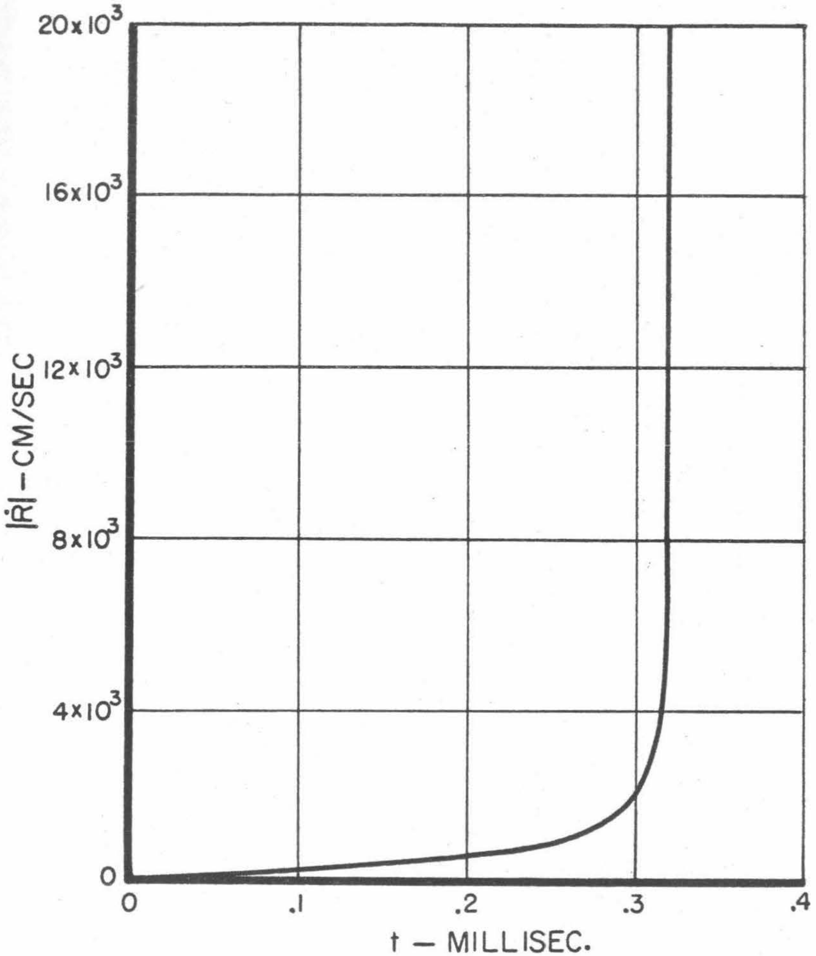

Fig. 12 - Magnitude of the radial velocity for the collapsing bubble of Fig. 11.

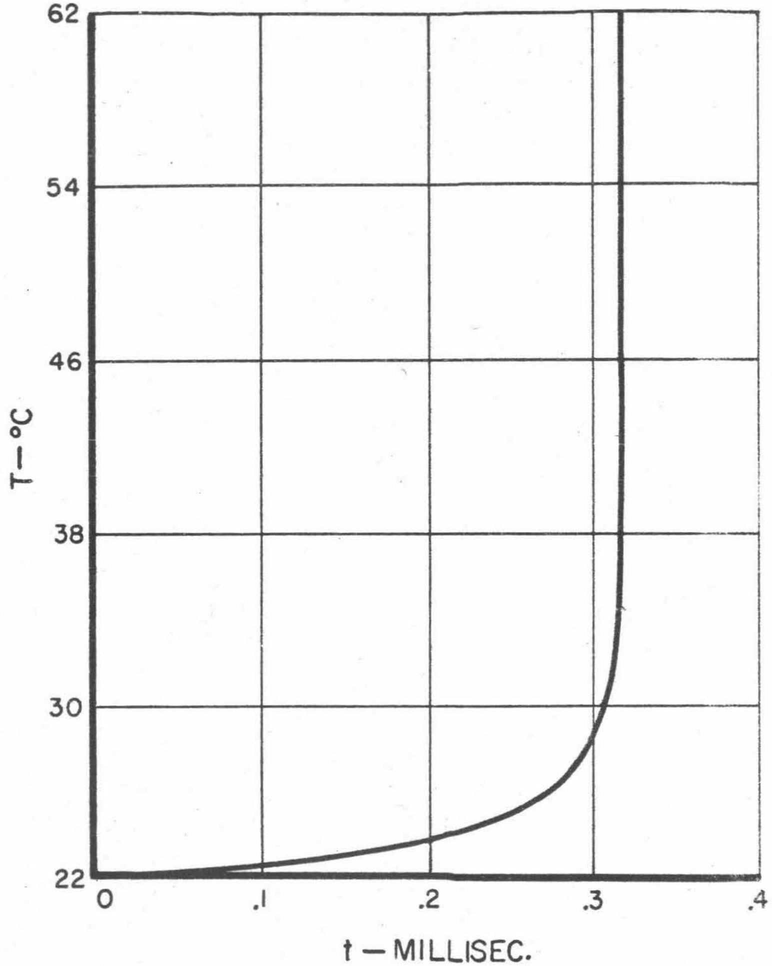

Fig. 13 - Temperature at the bubble wall for the bubble of Fig. 11.

APPENDIX

A. List of Physical Constants.

The tables below give representative values taken from E.N. Dorsey, Properties of Ordinary Water-Substance (Reinhold Publishing Corporation, New York, 1940). Values for the vapor are uncertain (experimentally) in the third significant figure and are somewhat dependent on pressure; those cited correspond to pressures of 1 atm. or below. Values for the liquid have been arbitrarily limited to four significant figures.

Water Vapor

$T\ ^\circ C$	0	100	150	200
$\eta \times 10^4$ gm/cm · sec	.884	1.26	1.44	1.62
$k \times 10^{-3}$ erg/cm · sec · $^\circ C$		2.38	2.68	3.03
$c_v \times 10^{-7}$ erg/gm · $^\circ C$	1.39	1.41	1.42	1.45
$\rho_{eq} \times 10^4$ gm/cc		5.98		
$D\ (= k/\rho_{eq}\, c_v)$ cm^2/sec		.282		

Gas constant per gm. of water vapor:

$$B = 1.386 \times 10^7 \text{ erg/gm} \cdot {}^\circ C.$$

Water

$T\ ^\circ C$	0	50	100	150	200
$\eta \times 10^3$ gm/cm · sec	17.94	5.49	2.84	1.86	1.36
$k \times 10^{-4}$ erg/cm · sec · $^\circ C$	5.54	6.43	6.80	6.85	6.66
$c_v \times 10^{-7}$ erg/gm · $^\circ C$	4.215	4.015	3.757		
$L \times 10^{-10}$ erg/gm	2.500	2.382	2.256	2.114	1.940
ρ gm/cc	.9999	.9880	.9583		
$\rho_{eq} \times 10^4$ gm/cc	.0485	.8302	5.977	25.48	78.62
$p_{eq} \times 10^{-6}$ $dynes/cm^2$	.006107	.1233	1.013	4.760	15.55
σ dynes/cm	75.6	67.9	58.8		
$D(= k/\rho c_v) \times 10^3$ cm^2/sec	1.31	1.62	1.89		

B. Evaluation of the Diffusion Integrals III(47b), (47c).

In terms of the new variable

$$t = \frac{1 - \sqrt{x}}{1 + \sqrt{x}} , \tag{a}$$

the integral III(47b)

$$I(\lambda) = \lambda \int_0^1 \frac{dx}{\sqrt{1 - x}} \left\{ e^{-\lambda^2 [\frac{1-\sqrt{x}}{1+\sqrt{x}}]} - e^{-\lambda^2 [\frac{1+\sqrt{x}}{1-\sqrt{x}}]} \right\} \tag{b}$$

becomes

$$I(\lambda) = 2\lambda \left\{ \int_0^1 \frac{1-t}{(1+t)^2} e^{-\lambda^2 t} \frac{dt}{\sqrt{t}} - \int_0^1 \frac{1-t}{(1+t)^2} e^{-\frac{\lambda^2}{t}} \frac{dt}{\sqrt{t}} \right\} . \tag{c}$$

The further substitution $t = 1/x$ in the second integral gives

$$\int_0^1 \frac{1-t}{(1+t)^2} e^{-\frac{\lambda^2}{t}} \frac{dt}{\sqrt{t}} = \int_1^\infty \frac{x-1}{(1+x)^2} e^{-\lambda^2 x} \frac{dx}{\sqrt{x}} ,$$

and therefore

$$\frac{1}{2\lambda} I(\lambda) = \int_0^\infty \frac{1-t}{(1+t)^2} e^{-\lambda^2 t} \frac{dt}{\sqrt{t}} ,$$

$$= [1 + \frac{d}{d(\lambda^2)}] \int_0^\infty e^{-\lambda^2 t} \frac{dt}{(1+t)^2 \sqrt{t}} . \tag{d}$$

Since

$$\frac{1}{(1+t)^2} = \int_0^\infty e^{-(1+t)x} x \, dx,$$

the integral in (d) may also be written

$$\int_0^\infty e^{-\lambda^2 t} \frac{dt}{\sqrt{t}} \int_0^\infty e^{-(1+t)x} x \, dx = \int_0^\infty e^{-x} x \, dx \int_0^\infty e^{-(x+\lambda^2)t} \frac{dt}{\sqrt{t}}$$

$$= \int_0^\infty e^{-x} x \sqrt{\frac{\pi}{x + \lambda^2}} \, dx, \tag{e}$$

after a change in the order of integration. By putting $y = x + \lambda^2$, one obtains after an integration by parts

$$\sqrt{\pi} \int_0^\infty e^{-x} \frac{x\,dx}{\sqrt{x+\lambda^2}} = \sqrt{\pi} \int_{\lambda^2}^\infty e^{-(y-\lambda^2)} (y-\lambda^2) \frac{dy}{\sqrt{y}}$$

$$= \sqrt{\pi}\,[\lambda + \tfrac{1}{2} e^{\lambda^2} \int_{\lambda^2}^\infty e^{-y} \frac{dy}{\sqrt{y}}] - \lambda^2 \sqrt{\pi}\, e^{\lambda^2} \int_{\lambda^2}^\infty e^{-y} \frac{dy}{\sqrt{y}}$$

$$= \lambda\sqrt{\pi} + \frac{\sqrt{\pi}}{2} (1 - 2\lambda^2)\, e^{\lambda^2} \int_{\lambda^2}^\infty e^{-y} \frac{dy}{\sqrt{y}}. \tag{f}$$

The use of (f) for the integral in (d) then gives

$$\frac{I(\lambda)}{2\lambda} = 2\lambda\sqrt{\pi} - 2\lambda^2\sqrt{\pi}\; e^{\lambda^2} \int_{\lambda^2}^\infty e^{-y} \frac{dy}{\sqrt{y}},$$

or

$$I(\lambda) = 4\lambda^2\sqrt{\pi} - 4\pi\lambda^3 e^{\lambda^2} \operatorname{erfc}(\lambda). \tag{g}$$

The asymptotic formulas for $I(\lambda)$ follow from the relations

$$\left.\begin{aligned} e^{\lambda^2} \operatorname{erfc}(\lambda) &\sim \frac{1}{\lambda\sqrt{\pi}} [1 - \frac{1}{2\lambda^2} + \frac{3}{4\lambda^4} - \cdots], \quad \lambda \to \infty, \\ \operatorname{erfc}(\lambda) &\sim 1 - \frac{2\lambda}{\sqrt{\pi}} [1 - \frac{\lambda^2}{3} + \frac{\lambda^4}{10} - \cdots], \quad \lambda \to 0. \end{aligned}\right\} \tag{h}$$

The integral III(47c)

$$I(\lambda) = \lambda \int_0^1 \frac{dx}{\sqrt{1-x}} \left\{ e^{-\lambda^2 [\frac{1-\sqrt{x}}{1+\sqrt{x}}]} \right.$$

$$\left. - \frac{\sqrt{\pi}}{2\lambda} \sqrt{\frac{1-x}{x}}\; e^{\frac{1-x}{4\lambda^2 x} + \frac{1}{\sqrt{x}} - 1} \operatorname{erfc}\left[\frac{1}{2\lambda}\sqrt{\frac{1-x}{x}} + \lambda\sqrt{\frac{1-\sqrt{x}}{1+\sqrt{x}}} \right] \right\} \tag{i}$$

may be transformed by the substitution

$$t = \sqrt{\frac{1 - \sqrt{x}}{1 + \sqrt{x}}} \tag{j}$$

to

$$I(\lambda) = 4\lambda \int_0^1 \frac{1-t^2}{(1+t^2)^2} e^{-\lambda^2 t^2} dt \left\{ 1 - \frac{\sqrt{\pi}}{\lambda} \frac{t}{1-t^2} e^{[\lambda t + \frac{t}{\lambda(1-t^2)}]^2} \right.$$

$$\left. \times \ \mathrm{erfc} \left[\lambda t + \frac{t}{\lambda(1-t^2)} \right] \right\} . \tag{k}$$

For $\lambda \ll 1$, $t < \lambda$,

$$\lambda t + \frac{t}{\lambda(1-t^2)} = \frac{t}{\lambda} + O(\lambda^2),$$

and the brace in (k) becomes

$$1 - \sqrt{\pi}\ (\tfrac{t}{\lambda})\ e^{(t/\lambda)^2} \mathrm{erfc}(\tfrac{t}{\lambda}) + O(\lambda^2). \tag{l}$$

As t in (k) increases beyond λ, the brace in (k) drops rapidly to zero $(\lambda \ll 1)$. But from eq. (h),

$$1 - \sqrt{\pi}\ (\tfrac{t}{\lambda})\ e^{(t/\lambda)^2} \mathrm{erfc}(\tfrac{t}{\lambda}) \sim \frac{1}{2} \frac{\lambda^2}{t^2} \quad \text{as} \quad t \to 1, \quad \lambda \ll 1,$$

so that for small λ the approximate expression (l) differs from the brace in (k) only in $O(\lambda^2)$ for the full range of t. Since the factor outside the brace is unity to $O(\lambda^2)$ when $t \approx \lambda$, an approximation to the integral which is valid to terms of relative order λ^2 is

$$4\lambda \int_0^1 dt \left\{ 1 - \sqrt{\pi}\ (\tfrac{t}{\lambda})\ e^{(t/\lambda)^2} \mathrm{erfc}\ (\tfrac{t}{\lambda}) \right\}$$

$$= 4\lambda - 2\lambda^2 \sqrt{\pi} \left\{ e^{1/\lambda^2} \mathrm{erfc}(\tfrac{1}{\lambda}) - 1 + \frac{2}{\lambda\sqrt{\pi}} \right\}.$$

Hence, by (h) again,

$$I(\lambda) \sim 2\sqrt{\pi}\,\lambda^2\,[1 - \frac{\lambda}{\sqrt{\pi}} + O(\lambda^2)] \quad \text{as} \quad \lambda \to 0. \tag{m}$$

For large λ the brace in (k) remains near unity until $t = 1 - O(1/\lambda^2)$, so that the dominant factor in the integral is $e^{-\lambda^2 t^2}$. It is convenient, therefore, to put

$$u = \frac{t}{1 - t^2}, \qquad x = \lambda t + \frac{u}{\lambda} \tag{n}$$

in (k), and write the integral as

$$I(\lambda) = 4\lambda \int_0^1 \frac{(1-t^2)}{(1+t^2)^2}\, e^{-\lambda^2 t^2}\, dt \left\{ 1 - \sqrt{\pi}\, \frac{u}{\lambda}\, e^{x^2}\, \operatorname{erfc}(x) \right\}. \tag{o}$$

In the region where $e^{-\lambda^2 t^2}$ is still large, u is of order $1/\lambda$ and x is of order unity. Thus in this region, we may expand

$$\operatorname{erfc}(x) = \operatorname{erfc}(\lambda t + \frac{u}{\lambda}) = \operatorname{erfc}(\lambda t) - \frac{2}{\sqrt{\pi}} \sum_{k=1}^{\infty} (\frac{u}{\lambda})^k \frac{[(\frac{d}{ds})^{k-1} e^{-s^2}]_{s=\lambda t}}{k!}$$

$$= \operatorname{erfc}(\lambda t) - \frac{2}{\sqrt{\pi}} e^{-\lambda^2 t^2} [(\frac{u}{\lambda}) - \lambda t (\frac{u}{\lambda})^2 + \cdots], \tag{p}$$

so that

$$\sqrt{\pi}\, \frac{u}{\lambda}\, e^{x^2} \operatorname{erfc}(x) = \frac{u}{\lambda}\, e^{2ut + u^2/\lambda^2} \Big\{ \sqrt{\pi}\, e^{\lambda^2 t^2} \operatorname{erfc}(\lambda t)$$

$$- 2[(\frac{u}{\lambda}) - \lambda t (\frac{u}{\lambda})^2 + \cdots] \Big\}. \tag{q}$$

By expanding u and the algebraic term in (o) in powers of $s \equiv \lambda t$ and combining terms, one obtains finally a relation

$$I(\lambda) \sim 4 \int_0^{\lambda} e^{-s^2}\, ds - \frac{4}{\lambda^2} \int_0^{\lambda} e^{-s^2} [\sqrt{\pi}\, s e^{s^2} \operatorname{erfc}(s) + 3s^2]\, ds$$

$$+ \frac{4}{\lambda^4} \int_0^{\lambda} e^{-s^2} [5s^4 + 2s^2]\, ds + O(1/\lambda^6). \tag{r}$$

The error involved in extending the integrals of (r) to $s = \infty$, rather than $s = \lambda$, is of order $e^{-\lambda^2}$, and so does not change the asymptotic expansion indicated by (r). By evaluating the integrals in (r), one finds

$$I(\lambda) \sim 2\sqrt{\pi}\ [1 - \frac{2}{\lambda^2} + \frac{19}{4\lambda^4} + 0(\frac{1}{\lambda^6})]. \qquad (s)$$

C. <u>Early Phase Temperature Integral IV(46).</u>

The substitution of the expansion

$$u = \frac{1}{\beta}\left\{\ln(Kw) + a_1 w + \frac{a_2}{2} w^2 + \cdots\right\} \tag{a}$$

into the temperature integral IV(40)

$$\mu \int_0^w \frac{e^v \, dv}{\sqrt{u(w) - u(v)}} = \mu w \int_0^1 \frac{e^{wv} \, dv}{\sqrt{u(w) - u(wv)}} \tag{b}$$

yields

$$\mu w \sqrt{\beta} \int_0^1 \frac{e^{wv} \, dv}{\sqrt{\ln \frac{1}{v} + a_1 w(1 - v) + \frac{a_2}{2} w^2(1 - v^2) + \cdots}}$$

$$= \mu w \sqrt{\beta} \int_0^1 \frac{dv}{\sqrt{\ln \frac{1}{v}}} \left\{ \frac{1 + wv + \frac{w^2 v^2}{2} + \cdots}{\sqrt{1 + a_1 w\left(\frac{1 - v}{\ln 1/v}\right) + \frac{a_2}{2} w^2\left(\frac{1 - v^2}{\ln 1/v}\right) + \cdots}} \right\}$$

$$= \mu w \sqrt{\beta} \left\{ \left[\int_0^1 \frac{dv}{(\ln 1/v)^{1/2}}\right] + w \left[\int_0^1 \frac{v \, dv}{(\ln 1/v)^{1/2}} - \frac{1}{2} a_1 \int_0^1 \frac{(1 - v) \, dv}{(\ln 1/v)^{3/2}}\right] \right.$$

$$+ \frac{w^2}{2} \left[\int_0^1 \frac{v^2 \, dv}{(\ln 1/v)^{1/2}} - a_1 \int_0^1 \frac{v(1-v) \, dv}{(\ln 1/v)^{3/2}} + \frac{3}{4} a_1^2 \int_0^1 \frac{(1-v)^2 \, dv}{(\ln 1/v)^{5/2}} \right.$$

$$\left.\left. - \frac{a_2}{2} \int_0^1 \frac{(1-v^2) \, dv}{(\ln 1/v)^{3/2}} \right] + \cdots \right\}, \tag{c}$$

valid for sufficiently small w.

Now, for $\mathrm{Re}(r)$, $\mathrm{Re}(s) > 0$,

$$\int_0^1 v^{r-1} \left(\ln \frac{1}{v}\right)^{s-1} dv = r^{-s}\,\Gamma(s). \tag{d}$$

Consider a typical integral in (c), for example that appearing in the coefficient of a_1 within the second bracket,

$$I = \int_0^1 \frac{(1-v)\,dv}{(\ln \frac{1}{v})^{3/2}} \quad . \tag{e}$$

If the exponent of the $\ln \frac{1}{v}$ factor were instead $1-s$, then for $\mathrm{Re}\,(s) > 0$, eq. (d) would give for I

$$\int_0^1 (1-v)\;(\ln \frac{1}{v})^{s-1}\; dv = [1 - (\tfrac{1}{2})^s]\;\Gamma(s). \tag{f}$$

But it is readily verified that both sides of eq. (f) are regular functions of the complex variable s for $\mathrm{Re}(s) > -1$, the singularity at $s = 0$ being only apparent. Therefore, by the theory of analytic continuation, the equality (f) remains valid for $\mathrm{Re}(s) > -1$. In particular, for $s = -1/2$, (f) gives

$$I = [1 - 2^{1/2}]\;\Gamma(-1/2). \tag{g}$$

The other integrals appearing in (c) may be similarly evaluted.

From eqs. (c), (d) one thus obtains

$$\mu \int_0^w \frac{e^v\,dv}{\sqrt{u(w) - u(v)}}$$

$$= \mu\, w \sqrt{\beta} \left\{ \Gamma(\tfrac{1}{2}) + w[2^{-1/2}\,\Gamma(\tfrac{1}{2}) - \tfrac{1}{2}\Gamma(-\tfrac{1}{2})\;(1 - 2^{1/2})\;a_1] \right.$$

$$+ \frac{w^2}{2}\,[3^{-1/2}\,\Gamma(\tfrac{1}{2}) - \Gamma(-\tfrac{1}{2})(2^{1/2} - 3^{1/2})a_1 + \tfrac{3}{4}\Gamma(-\tfrac{3}{2})(1 - 2\cdot 2^{3/2} + 3^{3/2})a_1^2$$

$$\left. - \tfrac{1}{2}\Gamma(-\tfrac{1}{2})\;(1 - 3^{1/2})\;a_2] + \cdots \right\}, \tag{h}$$

which reduces to eq. IV(46) on evaluating the gamma functions.

D. Asymptotic Phase Temperature Integral IV(59).

By differentiating eq. IV(58)

$$z(u) \sim \frac{2}{\pi\mu} \sqrt{u-u_o} \left\{ 1 + \frac{b_1}{(u-u_o)^{1/6}} + \cdots + \frac{b_5}{(u-u_o)^{5/6}} + b_6 \frac{\ln(u-u_o)}{u-u_o} \right\},$$

$$u > u_1, \qquad \text{(a)}$$

and substituting into the temperature integral IV(59) there results after a change of variable,

$$\mu \int_{u_1}^{u} \frac{z'(v)\, dv}{\sqrt{u-v}} \sim \frac{1}{\pi} \int_{\left(\frac{u_1-u_o}{u-u_o}\right)}^{1} \frac{dv}{\sqrt{v}\,\sqrt{1-v}} \left\{ 1 + \frac{1}{v^{1/6}} \left[\frac{2}{3} \frac{b_1}{(u-u_o)^{1/6}} \right] \right.$$

$$+ \frac{1}{v^{2/6}} \left[\frac{1}{3} \frac{b_2}{(u-u_o)^{2/6}} \right] + 0 - \frac{1}{v^{4/6}} \left[\frac{1}{3} \frac{b_4}{(u-u_o)^{4/6}} \right]$$

$$\left. - \frac{1}{v^{5/6}} \left[\frac{2}{3} \frac{b_5}{(u-u_o)^{5/6}} \right] - \frac{1}{v} \left[\ln v + \ln(u-u_o) - 2 \right] \left[\frac{b_6}{u-u_o} \right] \right\}. \qquad \text{(b)}$$

The terms in (b), except for the last one, yield hypergeometric-type integrals (incomplete Beta functions)

$$I_s(x) = \int_x^1 \frac{v^{s-1}\, dv}{\sqrt{1-v}} = \frac{1}{s} \left[F(\tfrac{1}{2}, s; s+1; 1) - x^s\, F(\tfrac{1}{2}, s; s+1; x) \right]; \qquad \text{(c)}$$

$$\sim \frac{\Gamma(\frac{1}{2})\, \Gamma(s)}{\Gamma(s + \frac{1}{2})} - \frac{1}{s} x^s \qquad \text{as} \qquad x \to 0^+, \qquad \text{(d)}$$

valid for $0 < x < 1$, $\mathrm{Re}(s) > 0$. Hence, by the theory of analytic continuation, (c) is valid provided only that $0 < x < 1$, $s \neq 0, -1, -2, \ldots$, and (d) holds when $\mathrm{Re}(s) > -1$, $0 < x < \infty$. For $s = 0$, (d) is meaningless, but may be defined by a limiting procedure. By differentiating (d) with respect to s at $s = -\frac{1}{2}$, one readily finds

$$\int_x^1 \frac{\ln v\, dv}{v^{3/2} \sqrt{1-v}} \sim -2\pi + \frac{2}{\sqrt{x}} [2 + \ln x] \quad \text{as} \quad x \to 0^+. \qquad \text{(e)}$$

Thus eqs. (d), (e) give for (b)

$$\mu \int_{u_1}^{u} \frac{z'(v)\,dv}{\sqrt{u - v}}$$

$$\sim \left\{ 1 + \frac{2}{3} \frac{\Gamma(\frac{2}{6})}{\Gamma(\frac{1}{2})\,\Gamma(\frac{5}{6})} \frac{b_1}{(u-u_o)^{1/6}} + \frac{1}{3} \frac{\Gamma(\frac{1}{6})}{\Gamma(\frac{1}{2})\,\Gamma(\frac{4}{6})} \frac{b_2}{(u-u_o)^{2/6}} \right.$$

$$\left. - \frac{1}{3} \frac{\Gamma(-\frac{1}{6})}{\Gamma(\frac{1}{2})\,\Gamma(\frac{2}{6})} \frac{b_4}{(u-u_o)^{4/6}} - \frac{2}{3} \frac{\Gamma(-\frac{2}{6})}{\Gamma(\frac{1}{2})\,\Gamma(\frac{1}{6})} \frac{b_5}{(u-u_o)^{5/6}} + 2\,\frac{b_6}{u-u_o} \right\}$$

$$- \frac{2}{\pi} \sqrt{\frac{u_1-u_o}{u-u_o}} \left\{ 1 + \frac{b_1}{(u_1-u_o)^{1/6}} + \frac{b_2}{(u_1-u_o)^{2/6}} + \frac{b_4}{(u_1-u_o)^{4/6}} \right.$$

$$\left. + \frac{b_5}{(u_1-u_o)^{5/6}} + b_6\,\frac{\ln(u_1-u_o)}{u_1-u_o} \right\} \qquad \text{(f)}$$

after a rearrangement, several terms cancelling. By comparison with eq. (a), the last group of terms in (f) is simply

$$+ \frac{1}{\sqrt{u-u_o}} \left[\frac{2}{\pi}\,b_3 - \mu z(u_1)\right] = \frac{1}{\sqrt{u-u_o}} \left(\frac{2}{\pi}\,b_3 - \mu\right),$$

since by assumption $z(u_1) = 1$. Eq. (f) reduces to eq. IV(59) of the text upon evaluation of the gamma functions.

E. Numerical Solution for the Collapsing Bubble.

The system IV(78) may be written

$$zz'' + \frac{7}{6} z'^2 + \frac{3}{z^{4/3}} [\frac{1}{z^{1/3}} + \phi] = 0, \tag{a}$$

$$\phi = \phi(\theta), \tag{b}$$

$$\xi z - 1 = \frac{2}{\pi \xi} \int_o^u \theta'(v) \sqrt{u - v} \, dv, \tag{c}$$

$$\xi = \xi(\theta); \tag{d}$$

$$z = 1, \quad z' = 0, \quad \theta = 0, \text{ at } u = 0. \tag{e}$$

In order to obtain a scheme for numerical integration, subdivide the range of values of u into intervals defined by the points

$$0 = u_o < u_1 \leq \cdots \leq u_k \leq \cdots \leq u_n < u_{n+1} < \cdots . \tag{f}$$

The intervals corresponding to (f) are in general not equal, but chosen as the integration proceeds. For convenience write

$$u_{n+1} - u_n \equiv h, \tag{g}$$

and assume that $z_k = z(u_k)$, $\theta_k = \theta(u_k)$, $\xi_k = \xi(\theta_k)$, $\phi_k = \phi(\theta_k)$ are known for $0 \leq k \leq n$.

If the interval $u_{k+1} - u_k$ is sufficiently short, $\theta'(u)$ within the interval may be approximated by

$$\nabla_k = \frac{\theta_{k+1} - \theta_k}{u_{k+1} - u_k} . \tag{h}$$

The integral in (c) evaluated at the point $u = u_{n+1}$ may then be estimated as

$$\int_o^{u_{n+1}} \theta'(v) \sqrt{u_{n+1} - v} \, dv = \sum_{k=o}^{n} \nabla_k \int_{u_k}^{u_{k+1}} \sqrt{u_{n+1} - v} \, dv$$

$$= \frac{2}{3} \sum_{k=o}^{n} \nabla_k [(u_{n+1} - u_k)^{3/2} - (u_{n+1} - u_{k+1})^{3/2}]. \tag{i}$$

Define

$$\left.\begin{aligned} I_o &= 0, \\ I_n &= \frac{4}{3\pi\zeta}\sum_{k=o}^{n-1} \nabla_k[(u_{n+1}-u_k)^{3/2} - (u_{n+1}-u_{k+1})^{3/2}]. \end{aligned}\right\} \qquad (j)$$

Then according to eqs. (i), (j) and (g), eq. (c) at $u = u_{n+1}$ becomes

$$\xi_{n+1}\, z_{n+1} - 1 = I_n + \frac{4\sqrt{h}}{3\pi\zeta}\,(\theta_{n+1} - \theta_n). \qquad (k)$$

The value of ξ_{n+1} in (k) may be estimated in terms of θ_{n+1} by an expansion of ξ about a value $\theta = \bar{\theta}$ near θ_{n+1} which uses equilibrium vapor density data, say

$$\xi_{n+1} = \xi(\theta_{n+1}) = \overline{\xi}\,[1 + \bar{d}_1(\theta_{n+1} - \bar{\theta}) + \bar{d}_2(\theta_{n+1} - \bar{\theta})^2 + \cdots]. \qquad (l)$$

Thus, for the first few steps of integration, $\bar{\theta} = 0$, and so $\overline{\xi} = 1$ initially. The temperature integral relation (k) becomes

$$z_{n+1}\,\overline{\xi}\,[1 + \bar{d}_1(\theta_{n+1} - \bar{\theta}) + \bar{d}_2(\theta_{n+1} - \bar{\theta})^2 + \cdots\,]$$

$$= 1 + I_n + \frac{4\sqrt{h}}{3\pi\zeta}\,[(\theta_{n+1} - \theta) - (\theta_n - \bar{\theta})], \qquad (m)$$

in which the only unknowns are θ_{n+1} and z_{n+1}. Eq. (m) is most easily solved for θ_{n+1} by an iteration procedure based on an alternative form of (m),

$$(\theta_{n+1} - \bar{\theta}) = \frac{z_{n+1}\overline{\xi} + \frac{4\sqrt{h}}{3\pi\zeta}(\theta_n - \bar{\theta}) - I_n - 1}{\frac{4\sqrt{h}}{3\pi\zeta} - z_{n+1}\,\overline{\xi}\,[\bar{d}_1 + \bar{d}_2(\theta_{n+1} - \bar{\theta}) + \cdots\,]}\;. \qquad (n)$$

To obtain z_{n+1}, the differential equation must be used. At each point $u = u_n$, make the approximations

$$\left.\begin{aligned} z''(u_n) &= \frac{\left(\dfrac{z_{n+1} - z_n}{u_{n+1} - u_n}\right) - \left(\dfrac{z_n - z_{n-1}}{u_n - u_{n-1}}\right)}{\frac{1}{2}\,(u_{n+1} - u_{n-1})}, \qquad \equiv z''_n\ ; \\ z'(u_n) &= \frac{1}{2}\left[\left(\frac{z_{n+1} - z_n}{u_{n+1} - u_n}\right) + \left(\frac{z_n - z_{n-1}}{u_n - u_{n-1}}\right) - \frac{1}{2}\, z''_n(u_{n+1} - 2u_n + u_{n-1})\right], \\ &\equiv z'_n . \end{aligned}\right\} \quad (o)$$

With these approximations, the formula

$$z(u) = z_n + (u - u_n)\, z'_n + \frac{(u - u_n)^2}{2}\, z''_n$$

is exact for $u = u_{n-1}, u_n, u_{n+1}$. When $(u_n - u_{n-1})$ equals $h = (u_{n+1} - u_n)$, eqs. (o) give

$$\left.\begin{aligned} z'_n &= \frac{z_{n+1} - z_{n-1}}{2h}, \\ z''_n &= \frac{z_{n+1} - 2z_n + z_{n-1}}{h^2}, \end{aligned}\right\} \quad (p)$$

so that the differential equation (a) at $u = u_n$ is approximated by the difference equation

$$z^2_{n+1} + [\tfrac{24}{7}\; z_n - 2z_{n-1}]\, z_{n+1} + \left[(z^2_{n-1} - \frac{48}{7}\, z^2_n + \frac{24}{7}\, z_n\, z_{n-1}) + \frac{72\, h^2}{7 z_n^{4/3}}\left(\frac{1}{z_n^{1/3}} + \phi_n\right)\right] = 0. \quad (q)$$

Given θ_n, eq. (q) may be solved for the positive root z_{n+1}, $\phi_n = \phi(\theta_n)$ being known from equilibrium vapor pressure data.

In order to keep the differences in z and θ small and ensure that a positive root z_{n+1} of the difference equation (q) exists, it becomes necessary to decrease h as the numerical integration proceeds. At the step where a new value of h is introduced, the approximations (o) rather than (p) must be used. The difference equation which applies at that step is therefore not (q), but one obtainable from (o).

To start the integration, a fictitious point $u_{-1} = - u_1$ is used. Corresponding to the initial condition $z'(0) = 0$ and the approximation (p), one must then choose $z_{-1} = z_1$. Since $z_o = 1$, the difference equation (q) for $n = 0$ simplifies to the linear equation

$$z_1 = 1 - \frac{3h^2}{2} (1 + \phi_o) \qquad (\phi_o \equiv \phi(\theta_o) \equiv \phi(0)). \tag{r}$$

The temperature equation becomes

$$\theta_1 = \frac{z_1 - 1}{\frac{4\sqrt{h}}{3\pi \overline{\xi}} - z_1(\bar{d}_1 + \bar{d}_2\,\theta_1 + \cdots)} \tag{s}$$

for $n = 0$, since $I_o = \theta_o = \bar{\theta} = 0$, $\overline{\xi} = 1$. For sufficiently small h, eq. (s) may be approximated by

$$\theta_1 = \frac{z_1 - 1}{\frac{4\sqrt{h}}{3\pi \overline{\xi}} - \bar{d}_1} \,. \tag{t}$$

It should be noted that $\overline{\xi}$, $\bar{d}_1$, $\bar{d}_2$, ... depend on $\bar{\theta}$, and change with each new expansion of $\xi(\theta)$. Because these parameters, as well as h, may be constant over several steps of integration, we have not given them indices which depend on u (i.e. on n).

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